

# REACTIVE INTERMEDIATES IN THE CHEMISTRY OF ACETYLARYLNITROSAMINES

Martin James Proctor Harger

A Thesis Submitted for the Degree of PhD  
at the  
University of St Andrews



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CHEMISTRY OF ACETYLARYLNITROSAMINES

A Thesis

presented for the degree of  
Doctor of Philosophy  
in the Faculty of Science of the  
University of St. Andrews

by

Martin James Procter Harger, B.Sc.

United College of St. Salvator  
and St. Leonard, St. Andrews.

September, 1968.





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I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor J.I.G. Cadogan since the 1st October 1965, the date of my admission as a research student.

I hereby certify that Martin James Procter Harger has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

ABSTRACT

The rôle of aryne intermediates in the reactions of acetylnitrosamines in solution has been investigated. Participation by 3-*t*-butylbenzyne in the decomposition of *o*-*t*-butyl-*N*-nitrosoacetanilide in benzene, leading to *m*-*t*-butylphenyl acetate, has been confirmed, although the major product, *o*-*t*-butylphenyl acetate, is formed predominantly from *o*-*t*-butylphenyl carbonium ions. 5-*t*-Butyl-1,4-dihydronaphthalene-1,4-endoxide has been isolated from the decomposition in the presence of furan. In common with the *o*-isomer, *m*- and *p*-*t*-butyl-*N*-nitrosoacetanilides yield 'aryne adducts' with 2,3,4,5-tetra-phenylcyclopentadienone in benzene. They do not, however, form *t*-butyl-1,4-dihydronaphthalene-1,4-endoxides with furan, and participation by a true aryne in their reactions, and in those of unsubstituted *N*-nitrosoacetanilide, is discounted. The nature of the arynoid intermediate has not, in spite of the elimination of many possibilities, been conclusively established, but it is probably the dipolar conjugate base formed by removal of an *o*-proton from the arenediazonium cation. Anomalies similar to those observed in the decomposition of *o*-*t*-butyl-*N*-nitrosoacetanilide are exhibited by 2,5-di-*t*-butyl-*N*-nitrosoacetanilide, which affords aryne adducts with

both furan and anthracene in greater yield than does the mono-substituted nitrosamide.

Aryne participation was not evident in the highly complex decompositions in benzene of 1,4-di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene, 2,5-di-*t*-butyl-1,3-di-(N-nitrosoacetamido)benzene, and 4-acetoxy-2,5-di-*t*-butyl-N-nitrosoacetanilide. Formation of 2,5-di-*t*-butylphenol, 2,5-di-*t*-butyl-p-benzoquinone, and acetic anhydride in the last-named reaction indicates deacetylation of the intermediate acetoxybenzenediazonium acetate, and suggests that complications in the reactions of the dinitrosamides arise from interaction between the N-nitrosoacetamido substituents. The decompositions of diphenyl[o-(N-nitrosoacetamido)phenyl] phosphine oxide and diethyl o-(N-nitrosoacetamido)phenylphosphonate have been studied, and evidence of aryne intermediacy obtained.

The results are discussed in terms of currently acceptable mechanisms for the decomposition of N-nitrosoacetanilide and, where necessary, modifications to these are suggested.

ACKNOWLEDGEMENTS

I should like to express my thanks to Professor J.I.G. Cadogan for suggesting the topic of research, and to Professor Cadogan and Dr. J.T. Sharp for their continued interest, advice, and encouragement throughout the three years in which the work was carried out.

My indebtedness to many members of the teaching, technical, and secretarial staffs of the Department of Chemistry in the University of St. Andrews, for their helpful suggestions and assistance at various times, is gratefully acknowledged.

In addition, I wish to record my thanks to Professor D.H. Hey, F.R.S. for a sample of 3-chlorobiphenyl, and to Professor Lord Tedder and British Petroleum Company Limited for recording mass spectra.

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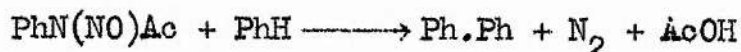
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PREAMBLE

The term 'radical', introduced by Lavoisier<sup>1</sup> in 1789, appeared frequently in chemical literature during the nineteenth century; but when it became possible to measure molecular weights, many of the supposed 'free radicals' - such as Kolbe's "Methyl"<sup>2</sup> and the "Ethyl" of Frankland<sup>3</sup> - were found to be dimeric. By 1890, few organic chemists were unwilling to accept the restrictions inherent in the Kekuléan concept of the quadrivalency of carbon, in return for the simplification of handling structural problems afforded by that theory.

In 1900 Gomberg<sup>4</sup> announced that his attempts to prepare hexaphenylethane had convinced him of the existence of a highly reactive free radical - triphenylmethyl. Paneth and Hofeditz<sup>5</sup> demonstrated the formation of gas-phase methyl radicals from the pyrolysis of tetramethyl-lead in 1929, but it was another five years before the important rôle of free radicals in liquid-phase reactions began to be appreciated.

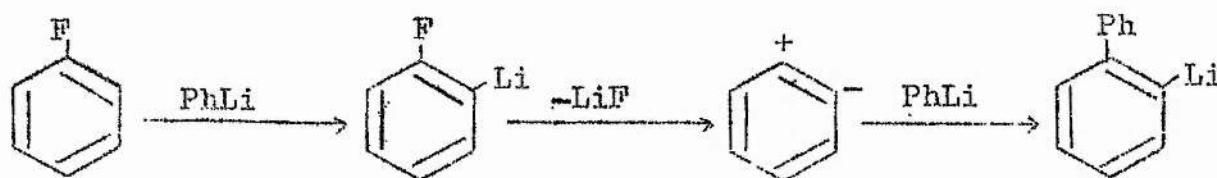
Bamberger<sup>6</sup> had shown in 1897 that when N-nitrosoacetanilide was allowed to decompose in benzene, nitrogen was evolved and biphenyl, together with acetic acid, was formed:



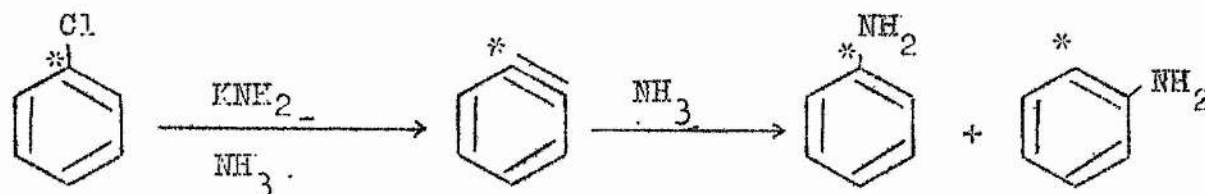
Grieve and Hey<sup>7</sup> now developed this reaction as a synthetic route to derivatives of biphenyl, using N-nitrosoacetanilide

with a variety of monosubstituted aromatic substrates. They found that the position at which substitution occurred depended little on the electronic character of the substituent - in marked contrast to such reactions as nitration and halogenation - and concluded that the reactive entity in these experiments was an electrically-neutral free phenyl radical. Succeeding years saw great advances in the field of radical chemistry - and in the use of acylarylnitrosamines as sources of aryl radicals. Cadogan and Hibbert<sup>8</sup> were surely justified in describing as anomalous the decomposition of o-t-butyl-N-nitrosoacetanilide when, in 1964, they discovered that this reaction gave products which could not be reconciled with the intermediacy of t-butylphenyl radicals, but rather, indicated participation by 3-t-butyl-1,2-dehydrobenzene.

A dehydrobenzene species ( $C_6H_4$ ) had been suggested as early as 1927,<sup>9</sup> but fifteen years passed before Wittig<sup>10</sup> successfully rationalised the exceptionally rapid formation of 2-lithiobiphenyl from fluorobenzene by invoking transient 1,2-dehydrobenzene - an intermediate in which he thought the charge to be permanently orientated:



Compelling evidence for the existence of 1,2-dehydrobenzene was presented by Roberts and his colleagues<sup>11</sup> who obtained equal amounts of two different isotopically-labelled anilines from  $[1-^{14}\text{C}]$  chlorobenzene:



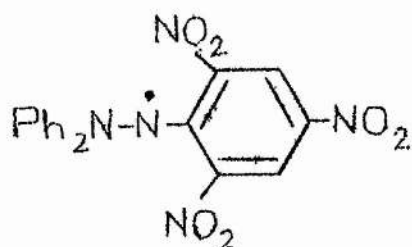
This result was clearly incompatible with Wittig's hypothesis of permanent charge-orientation in dehydrobenzene.

A prerequisite to discrimination between the parts played by dehydroaromatic species (arynes) and aryl radicals in the reactions of acylarylnitrosamines is a background knowledge of the chemistry of both these intermediates.

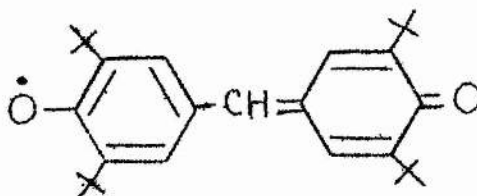
FREE RADICALS AND ARYNES

The lifetime of a chemical species is determined by one or other of two distinct factors: the intrinsic thermodynamic stability of the entity or, more frequently, its reactivity towards its environment. Many free radicals, such as methyl and phenyl, are short lived - but not unstable - because their high energy contents ensure that they will rapidly react with their surroundings. Paneth and Hofeditz<sup>5</sup> estimated a half-life of the order of one thousandth of a second for the methyl radical in their system. Other radicals, however, are unstable, and decompose spontaneously - thus the acetoxy radical gives a methyl radical and carbon dioxide.<sup>12,13</sup>

The triphenylmethyl radical, although stabilised by the delocalisation of its unpaired electron, has never been isolated as other than the dimer with which it is in equilibrium. It has been calculated that were it possible to obtain a one per cent solution of triphenylmethyl, it would be half dimerised in about one tenth of a second.<sup>14</sup> Some radicals, because of their resonance stabilisation and the steric hindrance to their combination, show little or no tendency to dimerise. Diphenylpicrylhydrazyl (I)<sup>15</sup> and "Galvinoxyl" (II)<sup>16</sup> are crystalline solids which can be kept exposed to the atmosphere



(I)

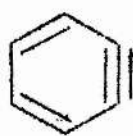


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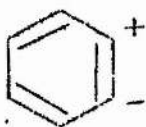
for many weeks without appreciable deterioration; and find use as scavengers for other radicals, particularly in radical chain reactions.<sup>17</sup>

Studies by Berry and his colleagues<sup>18,19,20</sup> have given some indication of the lifetime of gaseous-state benzyne. Flash photolysis of both benzenediazonium-2-carboxylate and o-iodophenylmercuric iodide allowed a continuous absorption spectrum - attributed to benzyne - to be observed for the duration of 200 microseconds.<sup>18,20</sup> Moreover, photolysis of the diazonium salt in a time-of-flight mass spectrometer produced an ion of mass 76 (dehydrobenzene), which had been replaced by one of mass 152 (biphenylene) within 250 microseconds.<sup>19,20</sup> The second-order rate constant for the dimerisation of benzyne under these conditions was estimated to be  $7 \times 10^8 \text{ l.mole}^{-1}\text{sec.}^{-1}$  - an extremely rapid process. The reactions of benzyne in solution are not generally accompanied by extensive dimerisation

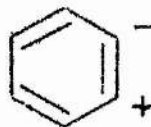
(but see reference 21), suggesting, perhaps, that in the liquid phase this intermediate enjoys a lifetime even shorter than that of gaseous benzyne. Four structures in which the six- $\pi$ -electron system is retained can be written for 1,2-dehydrobenzene:



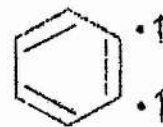
(III)



(IV)



(V)



(VI)

The  $sp^2$  orbitals released by removal of two ortho-substituents from benzene can overlap to form an 'acetylenic' bond (III): the extent of overlap will, however, be severely limited by the strain imposed on the ring. Both of the dipolar forms (IV,V) have an  $sp^2$  orbital containing two electrons with anti-parallel spins, while the parallel spins of the electrons in the diradical structure (VI) give rise to a triplet state. Wittig<sup>22</sup> now considers that the observed behaviour of benzyne in solution can best be reconciled with a resonance hybrid of the three singlet structures. The possibility that a triplet diradical structure may exist in the gas phase can not be discounted, and might account for the rapid dimerisation of gaseous benzyne. As long as the identity of the structures of liquid-state and gaseous-state dehydrobenzene remains in doubt, dissimilar behaviour in the

two phases can not, with certainty, be attributed solely to a difference in lifetime.

Attempts have been made to deduce some measure of the lifetime of liquid-phase benzyne from its selectivity in its chemical reactions with similar reagents. Thus Wittig<sup>22</sup> regarded the marked differences in the yields of the various halobenzenes formed by competitive addition of halide ion to benzyne in ethanol<sup>23</sup> as indicative of an appreciable lifetime for the intermediate; but other workers have remarked on the lack of discrimination shown by benzyne in its reactions with nucleophiles.<sup>24</sup>

The free radicals to be considered in this thesis are all electrically neutral; and their reactions, in contrast to ionic processes, are characterised by low sensitivity to the polarity of the reaction medium. Because of the minimal charge-separation in the transition state leading to homolysis, the rate of decomposition of t-butyl peroxide shows little variation in the gas phase and in solvents of widely different dielectric constant.<sup>25</sup> Polar factors can not, however, be entirely disregarded in radical reactions, as is shown by the dependence of the alternation of monomer units in a co-polymer on their relative polar properties.<sup>26a</sup> Further, Hey<sup>26b</sup> has suggested that the small differences in the ratios of the isomeric biaryls obtained with each of a variety of aryl radicals



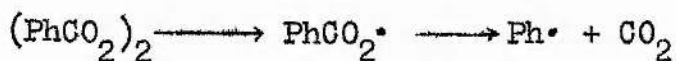
and a given substrate may be attributed (in part) to polar influences in the attacking radical. Although dehydrobenzene is also electrically neutral, the formation of a phosphonium betaine with triphenylphosphine demonstrates its ability to become highly polarised in the vicinity of a nucleophile:<sup>27</sup>



#### A. Sources of Aryl Radicals in Solution

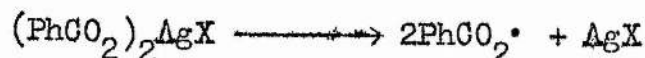
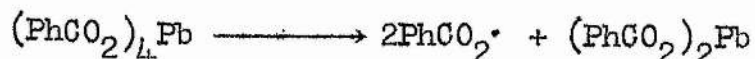
Homolysis of a molecule to yield free radicals will occur readily at a temperature below 150° provided the energy of activation does not exceed 40 kcal. per mole.

When a solution of dibenzoyl peroxide in a monosubstituted aromatic solvent ( $\text{C}_6\text{H}_5\text{R}$ ) is heated at 80°, carbon dioxide is evolved, and a mixture of isomeric biaryls ( $\text{PhC}_6\text{H}_4\text{R}$ ), formed through the intermediacy of the phenyl radical, results.<sup>28</sup>



Not all the benzoyloxy radicals produced by scission of the oxygen-oxygen bond fragment to phenyl radicals, as is evidenced by the formation of small amounts of benzoic acid and isomeric monosubstituted aryl benzoates ( $\text{PhCO}_2\text{C}_6\text{H}_4\text{R}$ ).<sup>29</sup>

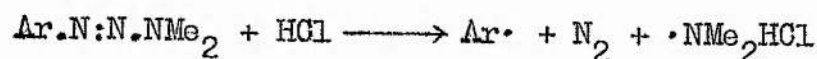
In similar manner the thermolyses of lead tetrabenzoate,<sup>30</sup> phenyliodoso benzoate,<sup>31</sup> and silver halide dibenzoates<sup>32</sup> yield phenyl radicals:



Azobenzene can be distilled without decomposition at 293°: an azo compound will undergo homolysis to an aryl radical only if this is accompanied by the formation of a less energetic radical, as in phenylazotriphenylmethane:<sup>28,33</sup>

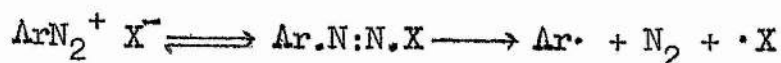


1-Aryl-3,3-dimethyltriazins are stable in hot benzene, but if hydrogen chloride is introduced into the solution, nitrogen is evolved and an aryl radical results:<sup>34</sup>

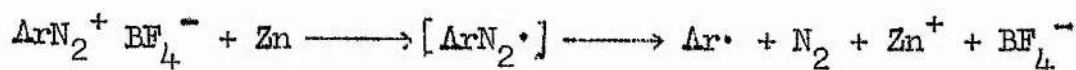


Diazonium salts such as the chloride<sup>35,36</sup> and tri-fluoroacetate<sup>37</sup> have been used to generate aryl radicals, which probably arise from the homolysis of the covalent diazo

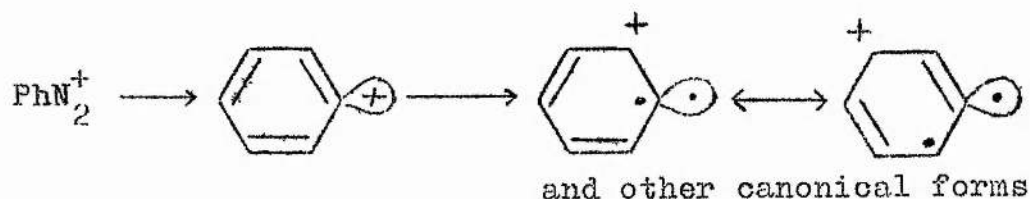
compound with which the salt is in equilibrium:



Phenyl radicals can be obtained from benzenediazonium fluoroborate in the presence of a metallic reducing agent such as zinc:<sup>38</sup>

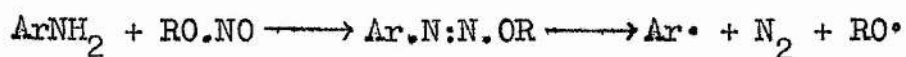


When benzenediazonium fluoroborate, in solution or suspension in an aromatic substance, is heated in the absence of a reducing agent, fluorobenzene is formed, together with small amounts of biaryl.<sup>39</sup> The ratio of the isomers of (for example) nitrobiphenyl produced in nitrobenzene differs greatly from that obtained using other sources of phenyl radical; and Abramovitch and his colleagues<sup>39</sup> have suggested that a highly electrophilic radical-ion is the arylating agent in these reactions:



Aryl radicals may conveniently be generated by the homogeneous, aprotic, diazotisation of the corresponding arylamine with pentyl nitrite.<sup>40,41</sup> Although the mechanism

has not been established, the radicals probably result from homolysis of the covalent diazoether:



Formation of aryl radicals in the decomposition of acylarylnitrosamines, and in the Gomberg reaction, will be discussed later.

Many molecules which are thermally quite stable can be made to dissociate by irradiation with ultraviolet light. Examples of compounds yielding aryl radicals in this way are diphenylmercury,<sup>42,43</sup> tetraphenyllead,<sup>43,44</sup> triphenylbismuth<sup>45</sup> and iodobenzene.<sup>43</sup>

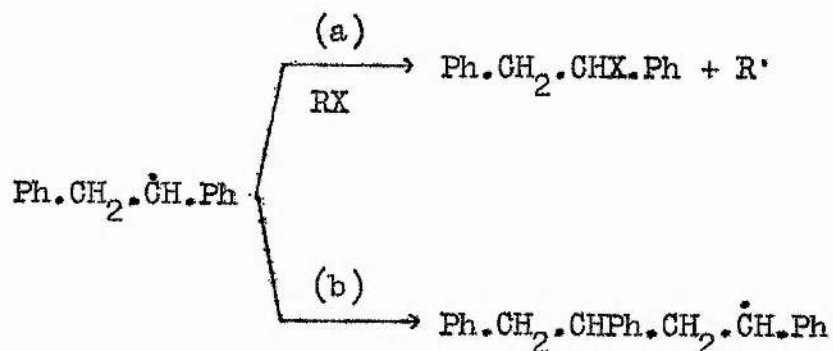
#### B. Reactions of Free Radicals in Solution

The great reactivity of most free radicals makes impossible an investigation of their liquid-phase reactions in a completely inert environment; so whenever possible, the substance to be subjected to radical attack is also employed as solvent.

When dibenzoyl peroxide is heated in carbon tetrachloride, the resulting phenyl radicals abstract chlorine from the solvent yielding chlorobenzene, and trichloromethyl radicals which may dimerise to hexachloroethane.<sup>46</sup> In chloroform, the phenyl radicals from either dibenzoyl peroxide or phenylazo-triphenylmethane abstract only hydrogen; but the reactive

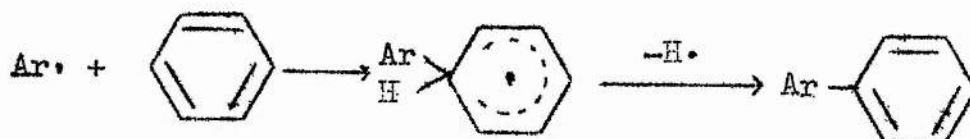
species from N-nitrosoacetanilide forms both benzene and chlorobenzene,<sup>47</sup> indicating that the reactions of a particular 'radical' are not always independent of its genesis. The decompositions of both phenylazotriphenylmethane and dibenzoyl peroxide in bromoform yield a mixture of benzene and bromobenzene, although not in the same ratio.<sup>47,48</sup>

If a molecule having an unsaturated centre - exemplified by the ethylenic bond in styrene - is present in the system, addition of an aryl radical may occur, forming a larger radical which can then react either by chain transfer (a), or by addition to another molecule of olefin (b), leading to telomeric or polymeric products:

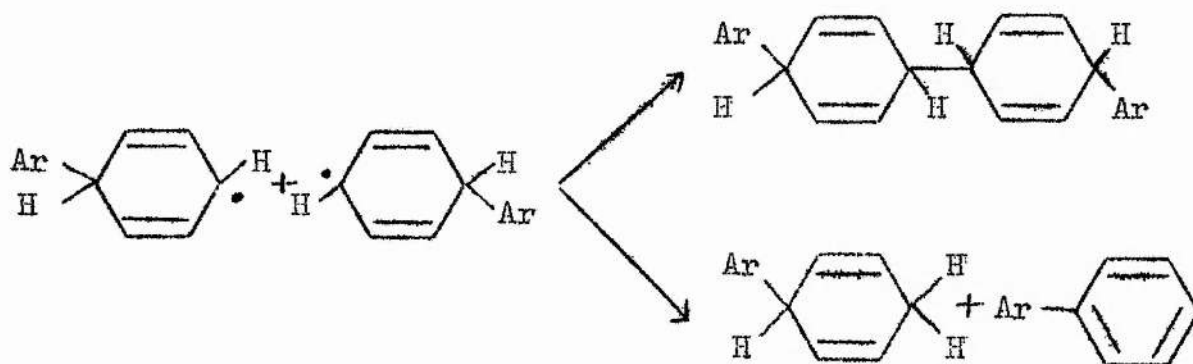


Aryl radicals in aliphatic solvents most commonly react by abstraction or addition; but in aromatic solvents, the major products are those formed by aromatic substitution, although even here the initial attack on the substrate is

additive,<sup>49</sup> e.g.



The arylcyclohexadienyl radical is converted to a biaryl when a hydrogen atom is abstracted by another radical; although because of its resonance stabilisation, it may (unlike the phenyl radical) exist long enough in solution to react by dimerisation or disproportionation,<sup>49b</sup> e.g.



Aryl radicals have recently been found to react with some aromatic solvents by abstraction<sup>50,51</sup> as well as by substitution. Thus, for example, the decomposition of di-*p*-chlorobenzoyl peroxide in iodobenzene yields *p*-chloriodobenzene in addition to the expected biaryls.<sup>50</sup>

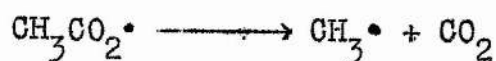
Simple substitution in which one radical displaces another from the substrate, although not common, is sometimes

observed, e.g.<sup>52</sup>

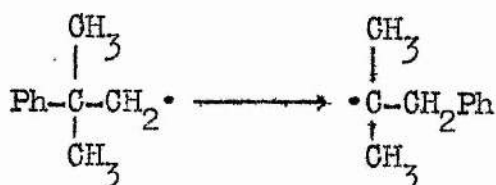


As well as reacting with another radical or molecule, some unstable free radicals can react in isolation by fragmentation or by rearrangement to a more stable radical.

e.g.<sup>12,13</sup>



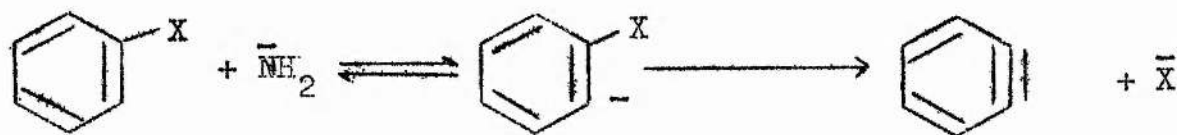
e.g.<sup>53</sup>



### C. Sources of Arynes in Solution

Simple aryl halides were used as sources of benzyne by Wittig<sup>10</sup> and by Roberts and his colleagues<sup>11,54</sup> in their early investigations, accomplishing dehydrohalogenation with, respectively, phenyl-lithium, and potassium amide in liquid ammonia. Fluorobenzene is aminated immeasurably slowly in liquid ammonia,<sup>55</sup> but reacts with phenyl-lithium to form benzyne more rapidly than do the other halobenzenes:<sup>10</sup> the mechanisms of these two reactions clearly must be different.

In strong base, a proton is removed from the halobenzene in an equilibrium process, and this may be followed by elimination of a halide ion:<sup>11b</sup>



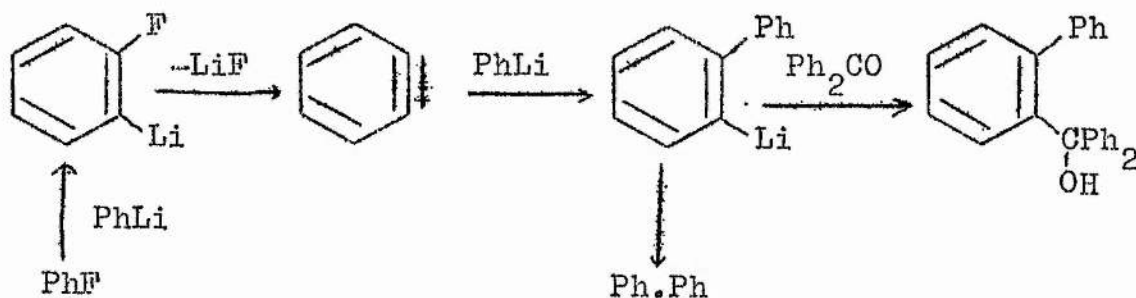
Fluorobenzene rapidly forms the carbanion, but halide elimination is very slow; in contrast to the reactions of bromo- and iodo-benzene where fast elimination follows deprotonation in the rate determining step. Both stages of the reaction occur at similar rates for chlorobenzene.<sup>11b,54</sup>

Arynes can be generated from aryl halides with potassium *t*-butoxide in an inert solvent, but the reaction proceeds at a useful rate only at temperatures above 140°. <sup>56</sup> The use of dimethyl sulphoxide as solvent allows the reaction to be carried out at room temperature, <sup>57</sup> but the aryne so formed reacts to some extent with this solvent. <sup>58,59</sup>

Wittig<sup>10</sup> suggested that the formation of benzyne from fluorobenzene and phenyl-lithium proceeded by way of a substitution-elimination reaction similar to that which had been observed in the dehydrochlorination of  $\omega$ -chlorostyrene. <sup>60</sup> Although the product he isolated was biphenyl, he inferred the intermediacy of 2-lithiobiphenyl from the formation of



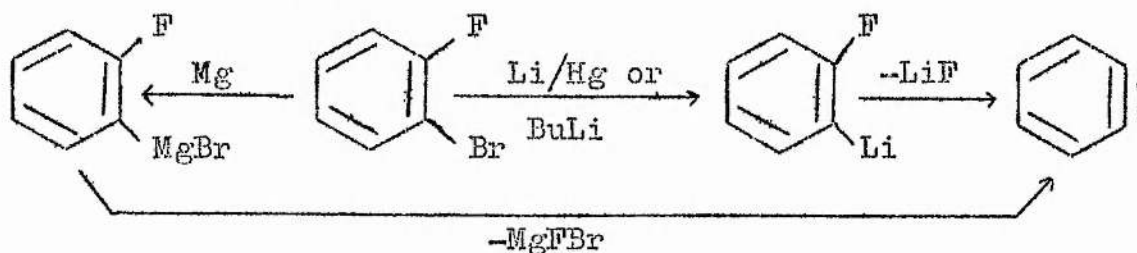
a carbinol when the reaction was repeated in the presence of benzophenone:<sup>61</sup>



*o*-Fluorolithiobenzene has since been isolated.<sup>62</sup> Phenyl-lithium can be replaced in benzyne-generating reactions by its complex with pentaphenylantimony, which dissociates reversibly, allowing the reagent to be present in high dilution<sup>63</sup> - an advantage when studying the reaction of benzyne with some other molecule which must compete with phenyl-lithium for the intermediate.

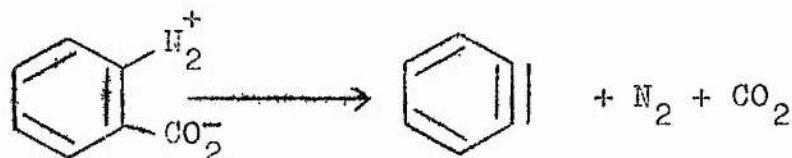


*o*-Dihalobenzenes liberate benzyne under mild conditions by reaction with lithium amalgam,<sup>64,65</sup> with magnesium,<sup>65,66</sup> and with butyl-lithium;<sup>62</sup> substitution or addition giving first an organometallic compound from which a metal halide is then eliminated, e.g.



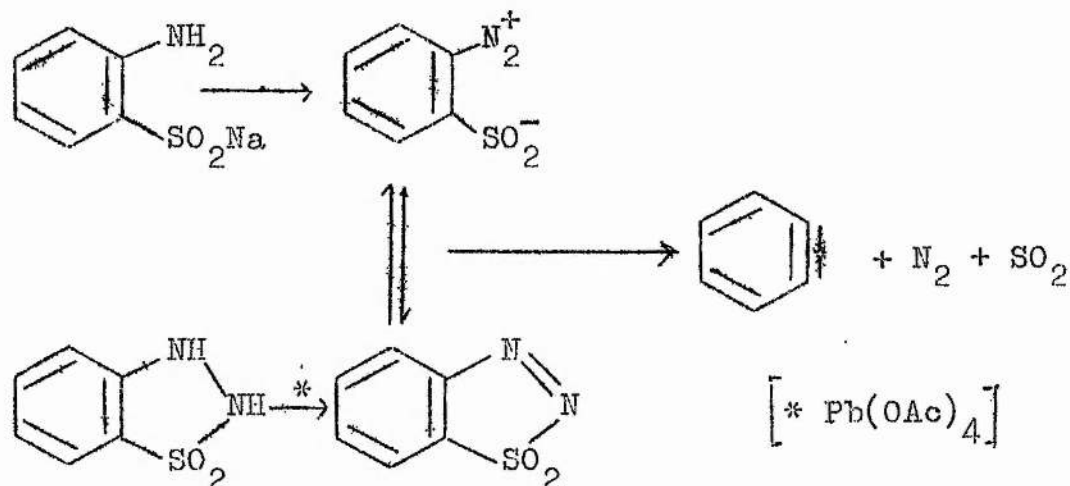
Several methods are now available for the formation of dehydroaromatic intermediates in the absence both of strong base and of metallic reagents, allowing the reactions of benzyne with, for example, carboxylic acids to be studied.

Nitrogen and carbon dioxide are evolved slowly from a solution or suspension of benzenediazonium-2-carboxylate (isolated as the inner salt) in an aprotic solvent at room temperature;<sup>67,68,69</sup>

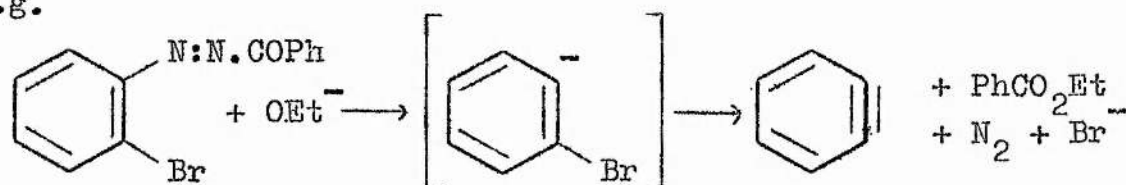


Isolation of the explosive diazonium salt is avoided in Friedman and Logullo's<sup>70</sup> modification of this reaction - in situ diazotisation of anthranilic acid with pentyl nitrite.

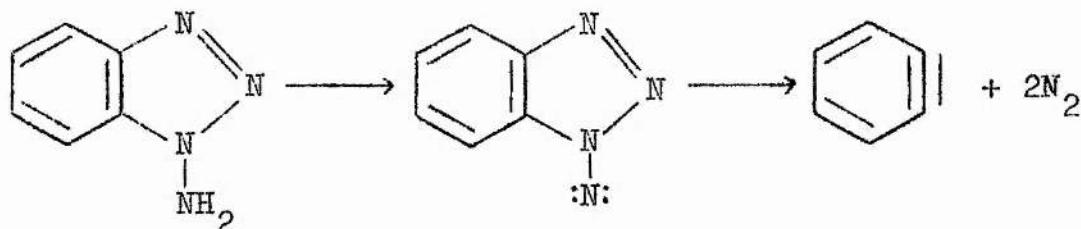
An analogous route to dehydrobenzene has been used extensively by Wittig and Hoffmann:<sup>23,71,80</sup>



Carbon dioxide is eliminated, and benzyne formed, in the thermolysis of diphenyliodonium-2-carboxylate,<sup>72,73,74</sup> and of the metal salts of *o*-halobenzoic acids,<sup>75,76</sup> while nitrogen is evolved during the heterolytic fragmentation of 2-halobenzeneazocarboxylates<sup>77</sup> and 2-halobenzeneazoketones,<sup>77</sup> e.g.



Oxidation of 1-aminobenzotriazole produces benzyne, possibly by decomposition of an intermediate nitrene:<sup>21,78</sup>

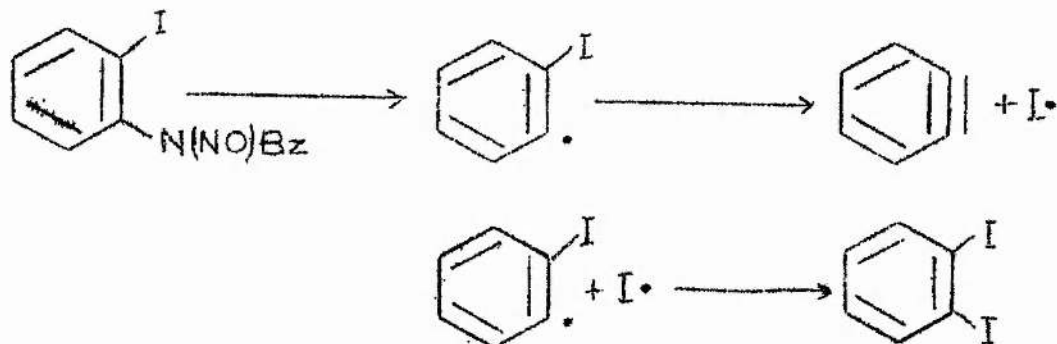


The extensive dimerisation to biphenylene which occurs when lead tetra-acetate is used as oxidising agent has been attributed to the aryne being in a triplet state,<sup>21</sup> but since similar behaviour is not observed with other oxidants, this explanation is now thought unlikely.<sup>79</sup>

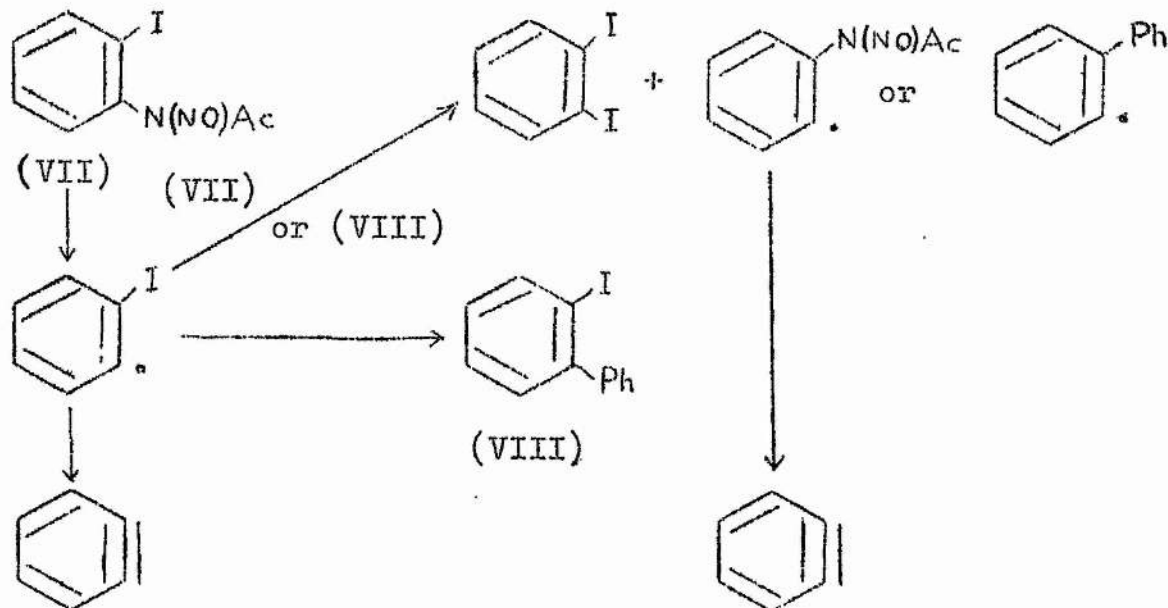
Benzenediazonium-2-carboxylate,<sup>18,20</sup> 1,2,3-benzothiadazole-1,1-dioxide<sup>80</sup> and *o*-di-iodobenzene<sup>81,82</sup> all yield benzyne on photolysis.

The decompositions in benzene of both *N*-(2-iodophenyl)-*N*-nitrosobenzamide<sup>83</sup> and *o*-iodo-*N*-nitrosoacetanilide<sup>50</sup> are reported to give benzyne together with *o*-di-iodobenzene

(and normal radical products). Kampmeir and Rubin<sup>83</sup> have suggested the following mechanism:



Brydon and Cadogan,<sup>50</sup> having shown that aryl radicals can abstract iodine from aryl iodides, argue that the formation of o-di-iodobenzene need not be linked with the appearance of benzyne:



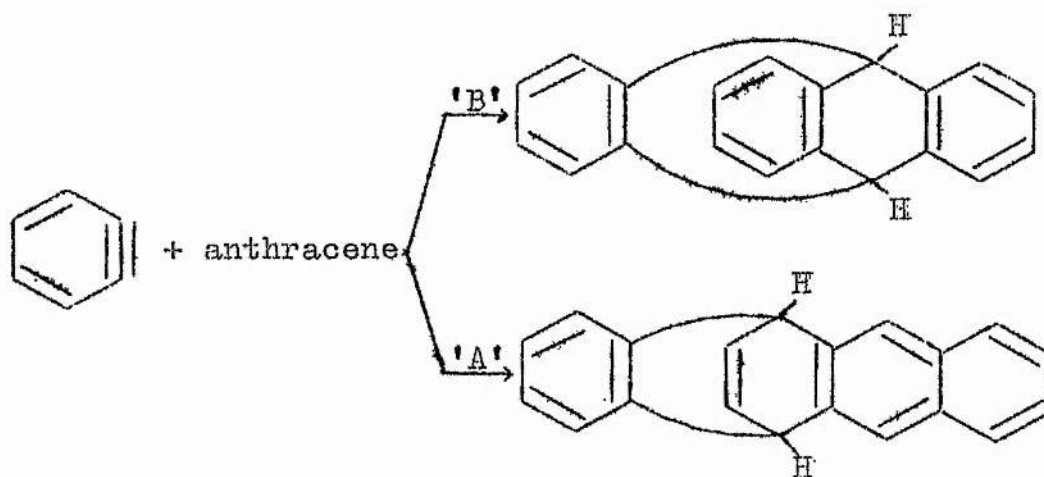
Participation by 3-*t*-butylbenzyne in the decomposition of o-*t*-butyl-N-nitrosoacetanilide is discussed in a later section of this Introduction.

### D. Reactions of Arynes in Solution

Most - though by no means all - of the reactions of benzyne may be rationalised by regarding this intermediate either as a powerful electrophile or as a strained, and therefore highly reactive, acetylene. Considered as the latter, benzyne might be expected to enter readily into cycloaddition reactions, and this indeed is the case.

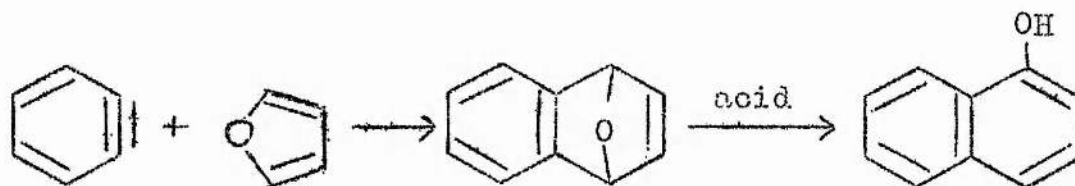
#### 1. Cycloaddition Reactions of Benzyne

Diels-Alder addition of aryne intermediates to the B-ring of anthracene provides a convenient route to triptycene and its substituted derivatives.<sup>66,70,84</sup> Reaction may also occur at one of the A-rings, especially when electrophilic substituents at position 9 and 10 reduce the electron density in ring B.<sup>85</sup>



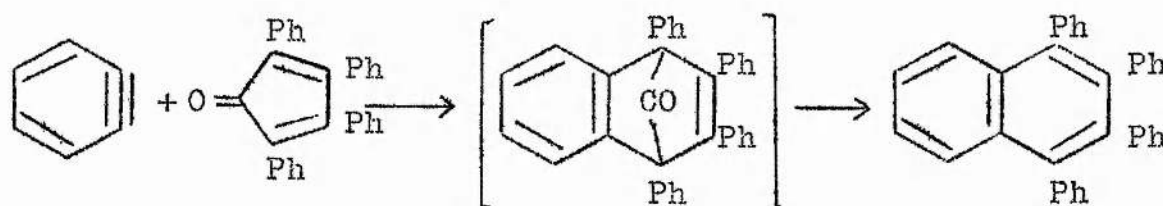
Furan is frequently employed as both the diene component and the solvent in 1,4-cycloaddition reactions;<sup>64,65</sup> care, however, must accompany its use for diagnosing benzyne

intermediacy in a system because the adduct - 1,4-dihydro-naphthalene-1,4-endoxide - readily isomerises under mildly acidic conditions:<sup>64</sup>



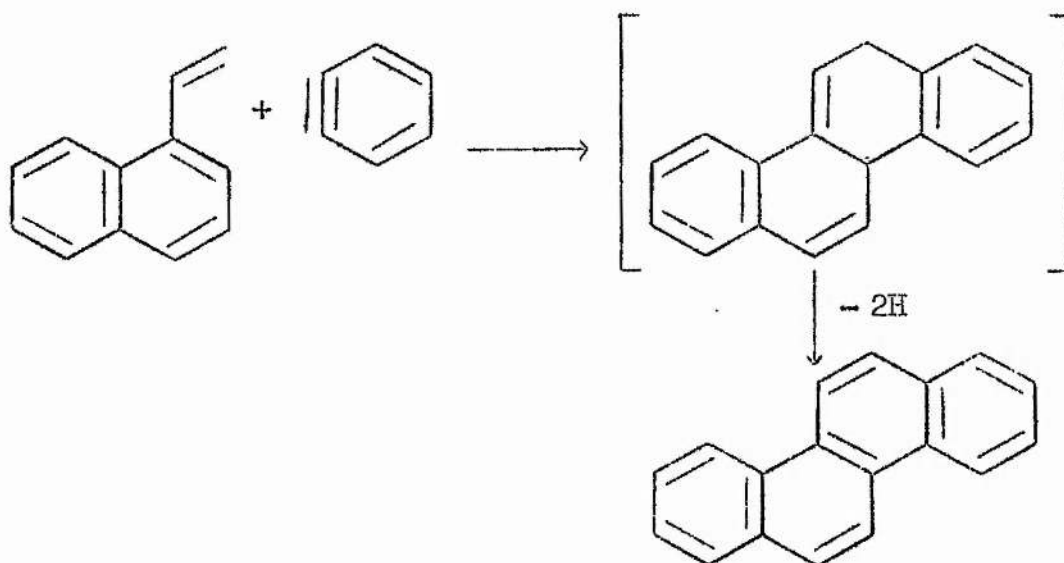
2-Methylfuran,<sup>86</sup> 2,5-dimethylfuran,<sup>70,86,87</sup> 1,3-diphenylisobenzofuran<sup>73</sup> and tetraphenylfuran<sup>88</sup> all react similarly with dehydroaromatic intermediates.

When 2,3,4,5-tetraphenylcyclopentadienone reacts with benzyne, carbon monoxide is eliminated and the product, usually isolated in high yield, is 1,2,3,4-tetraphenylnaphthalene:<sup>72,73,88</sup>



As might be predicted, the yield of adduct is even greater when electron-repelling substituents in the ketone increase the electron density of the five membered ring as, for example, in 2,5-di-*p*-anisyl-3,4-diphenylcyclopentadienone.<sup>73</sup>

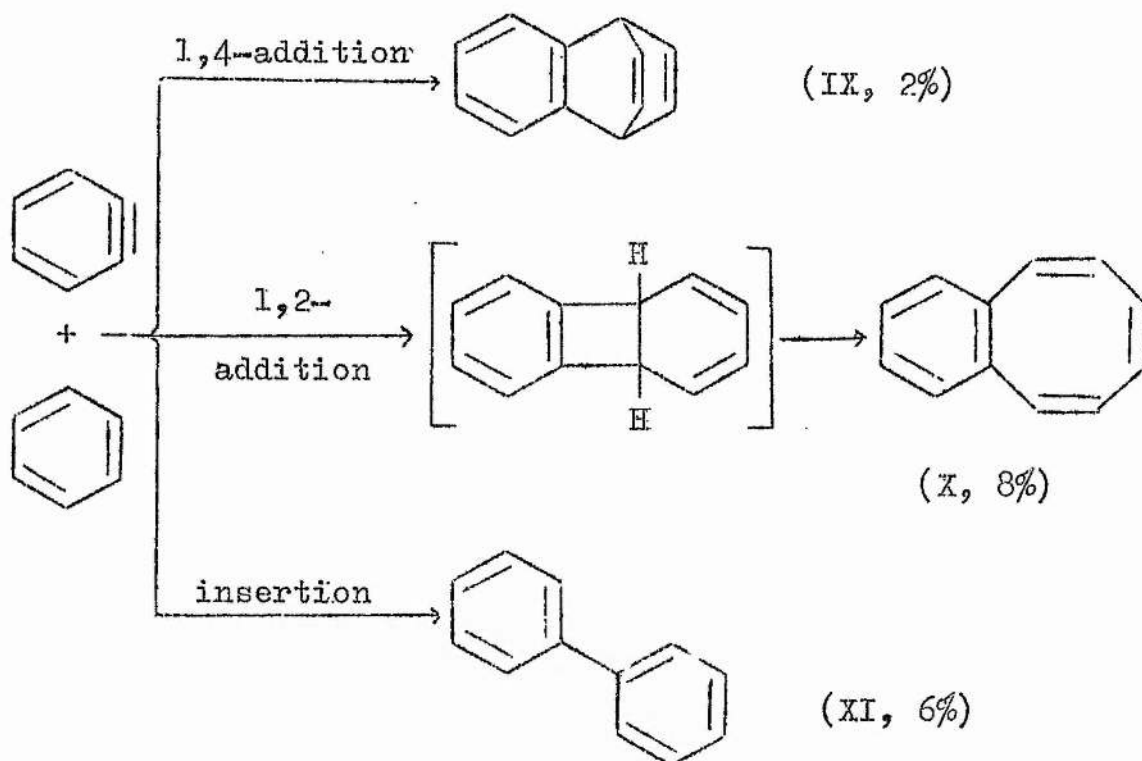
Although few instances of 1,4-cycloaddition of an aryne to an acyclic diene are known,<sup>89</sup> the reactions of benzyne with both styrene<sup>90</sup> and 1-vinylnaphthalene<sup>91</sup> involve the acyclic double bonds, e.g.



Other dienes - notably pyrrole and its derivatives<sup>92</sup> - form Diels-Alder adducts with benzyne, but as these reactions are of synthetic rather than diagnostic value, they will not be considered here. Brief reference should, however, be made to the evidence presented by Huisgen and Knorr<sup>93</sup> for the identity of the benzyne from different sources, viz. the invariance of the product ratio in its competitive addition to cyclohexa-1,3-diene and furan.

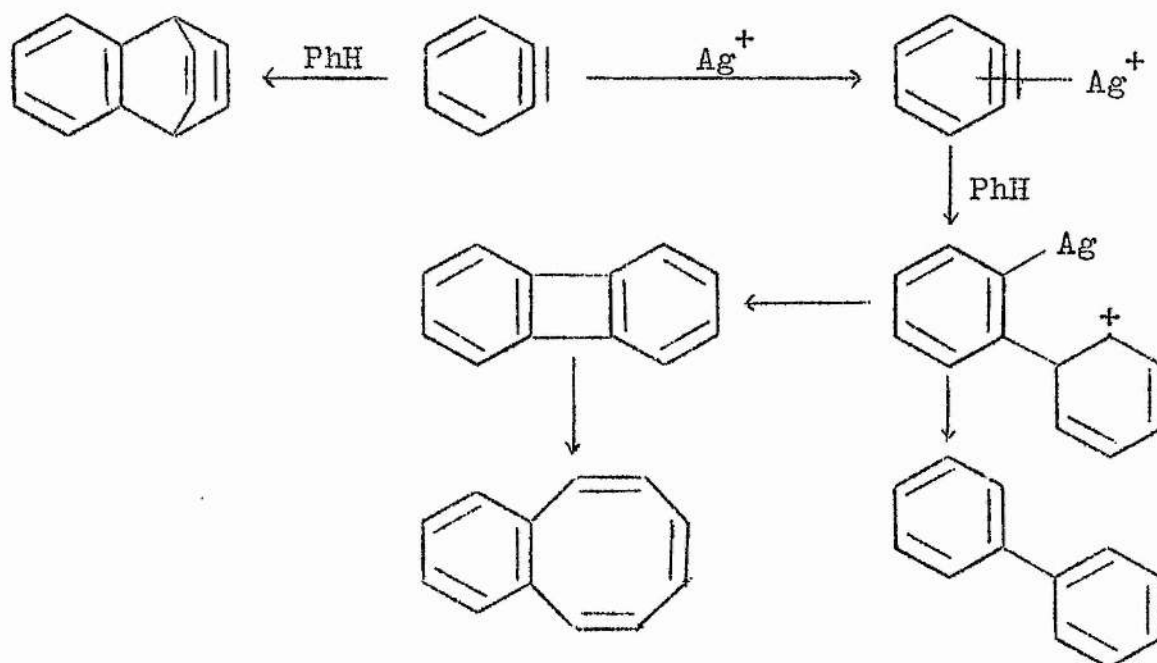
Benzene, although formally a diene, is not generally reactive towards dienophiles, and is often used as an 'inert' solvent for aryne reactions; it will, however, in the absence of any more reactive arynophile, react with dehydrobenzene. Miller and Stiles<sup>67,69</sup> allowed benzenediazonium-2-carboxylate to decompose in pure benzene, and identified among the products benzobicyclo[2,2,2]octatriene (IX),

benzocyclo-octatetraene (X) and biphenyl (XI).

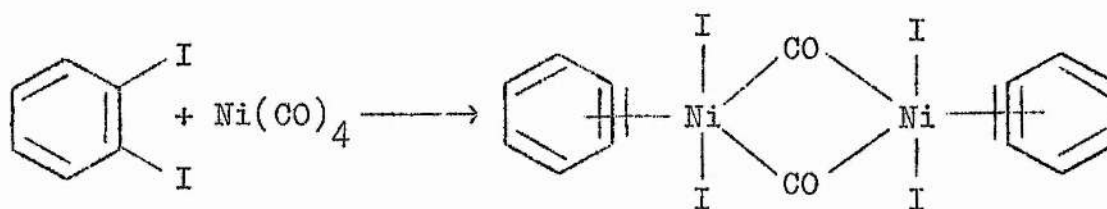


When Friedman<sup>94</sup> executed a similar experiment he found only trace amounts of benzocyclo-octatetraene and biphenyl, the major products being benzobicyclo[2,2,2]octatriene (17%) and biphonylene (2%). He reasoned that the discrepancies between the two sets of results might arise from contamination of Miller and Stiles' diazonium salt with silver ions (that had been used in its isolation, but which were absent from his own preparation), which could compete with benzene for the aryne:

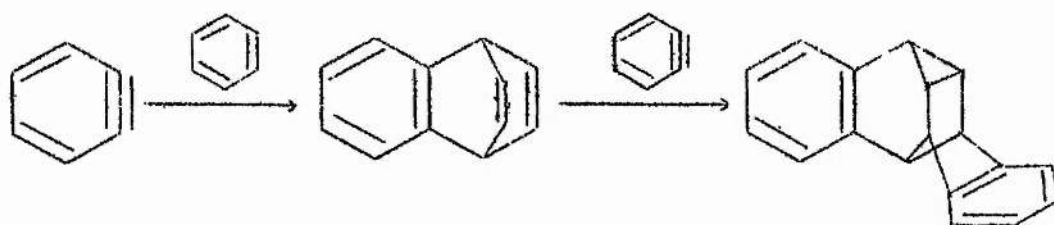




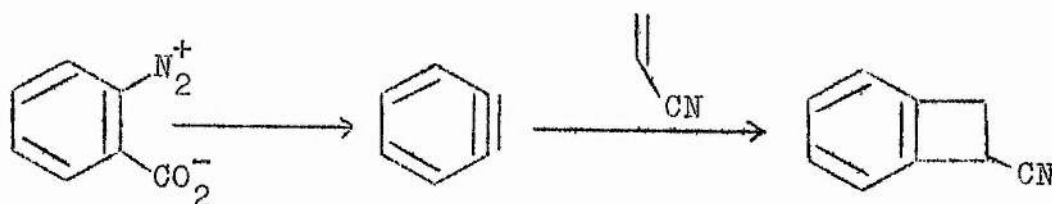
To test his theory, Friedman<sup>94</sup> repeated his reaction in the presence of trace amounts of silver salts, and observed a decrease in the yield of benzobicyclo[2,2,2]octatriene, and a corresponding increase in the total yield of the other products. Having shown that none of the compounds isomerised under the influence of silver ions, his theory appeared to be vindicated. Although no other ions have been found which influence its reactions in this way, a stable complex of benzyne, formed from o-di-iodobenzene and nickel tetracarbonyl, has been reported:<sup>95</sup>



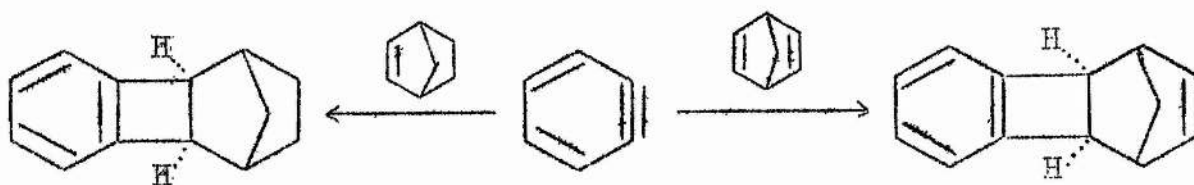
A product arising from the addition of two benzyne entities to one molecule of benzene has been indentified:<sup>94,96</sup>



From these experiments it is apparent that 1,2-cycloaddition of benzyne to benzene occurs (appreciably) only in the presence of silver ion. Benzocyclobutane derivatives have been obtained with ethyl vinyl ether,<sup>97</sup> vinyl acetate,<sup>97</sup> acrylonitrile,<sup>98</sup> and ethyl acrylate;<sup>98</sup> in all cases the benzyne precursor being benzenediazonium-2-carboxylate, e.g.



Since the method of preparation of the diazonium salt is not recorded, it is a matter for conjecture whether or not these 1,2-cycloaddition reactions also depend on the presence of silver ions. This is not the case, however, in the reactions of benzyne (formed from the Grignard reagent) with bicyclo[2,2,1] heptene and bicyclo[2,2,1] heptadiene.<sup>99</sup>



A high yield of 1-phenylbenzotriazole results from the 1,3-cycloaddition of benzyne to phenyl azide:<sup>71</sup>

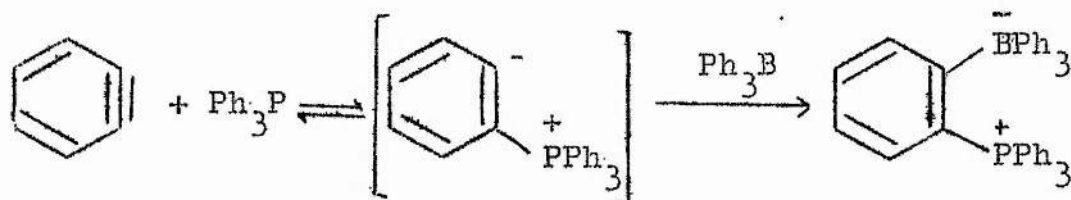


Many other azides - both aromatic and aliphatic - react similarly,<sup>100,101</sup> as do also benzonitrile oxide<sup>102</sup> and a number of diazoketones.<sup>103</sup>

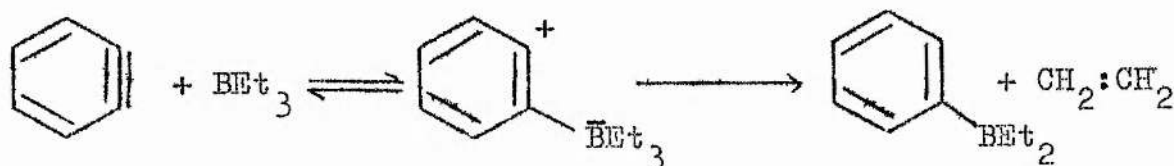
## 2. Reactions of Benzyne with Nucleophiles and Electrophiles

Aniline is formed in the reaction of bromobenzene with sodamide in liquid ammonia by way of nucleophilic attack by amide ion on the intermediate dehydrobenzene. If a weak acid is introduced to the system, removal of a proton gives the conjugate base, which will then compete with the amide ions for benzyne.<sup>24,104</sup> The competitive efficiency of these anions is not, however, necessarily related to their base strength or nucleophilicity as measured in other reactions. Thus, for example, Scardaglia and Roberts<sup>24</sup> found that addition of phenol ( $pK_a$  10.0) to the system gave only 4% diphenyl ether, while 42% diphenyl sulphide resulted from the addition of thiophenol ( $pK_a$  8.4).

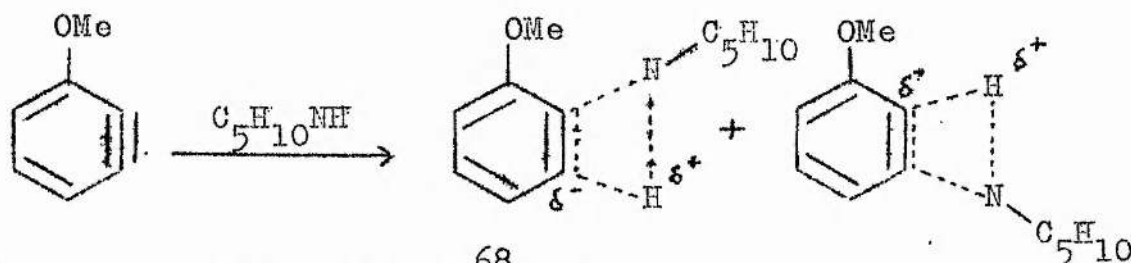
Nucleophilic attack by triphenylphosphine on benzyne results in 9-phenyl-9-phosphafluorene;<sup>105</sup> but if an electrophile such as triphenylboron is also present, the product is a betaine;<sup>27</sup>



Although comparatively rare, electrophilic attack on benzyne can occur, as in its reaction with triethylboron:<sup>27</sup>

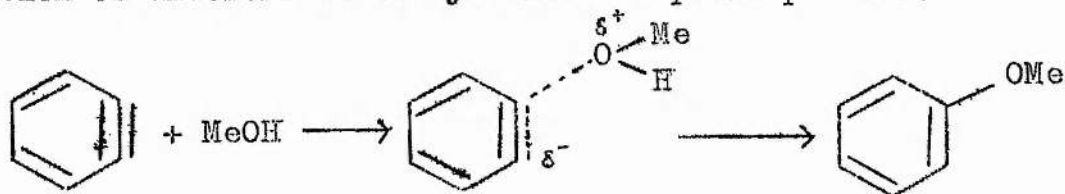


A concerted four-centre mechanism has been proposed for the additions of piperidine<sup>106</sup> and ethanol<sup>80,107</sup> to dehydroaromatic intermediates, e.g.



Stiles, Miller and Burckhardt<sup>68</sup> reasoned that since *t*-butyl phenyl ether resulted from the decomposition of benzene-diazonium-2-carboxylate in *t*-butanol, but had been reported (by other workers<sup>24</sup>) to be absent from the products of the reaction of bromobenzene with potassium amide in the

presence of t-butoxide anion\* it was unlikely that the addition of t-butanol to benzyne proceeded through simple nucleophilic attack. Moreover, they demonstrated that benzoic acid would add to benzyne to give phenyl benzoate; and that the competitive addition of pairs of aromatic carboxylic acids depended little on the relative strength of the acids. Bunnett and his co-workers<sup>108</sup> have since shown, however, that when 4-chlorobenzyne is generated in methanol containing increasing concentrations of methoxide ion, the para-to-meta ratio of the resulting chloroanisole decreases from five to two. Such observations - that methoxide ion is more reactive than methanol towards arynes, and that the orientating effect is greater for the addition of neutral methanol - lead to the conclusion that the addition of alcohols to benzyne is a stepwise process:<sup>108</sup>



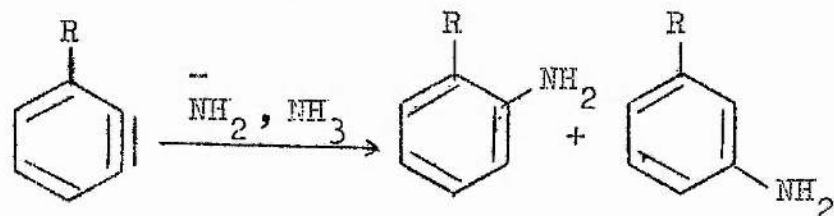

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\* It should be noted that aryl halides react with potassium t-butoxide in the absence of added alcohol to give (in high yield) aryl t-butyl ethers via an aryne intermediate.<sup>56</sup>

The mechanism by which carboxylic acids add to arynes remains in doubt.

### 3. Reactions of Substituted Benzyne

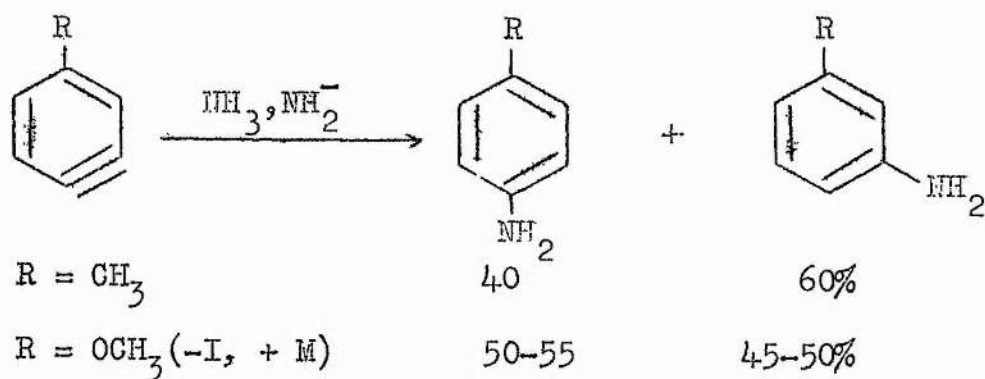
A monosubstituted benzyne is, of necessity, unsymmetrical; and since the dehydro bond is not permanently orientated, non-cyclic addition will usually give two products, in a ratio determined largely by the nature of the substituent. Some representative results from the experiments of de Graff, den Hertog and Melger<sup>109</sup> illustrate the principles that have emerged from the investigations of many workers into the reactions of arynes with nucleophiles. In these examples the benzyne precursors are the aryl bromides, and the figures represent relative yields only.



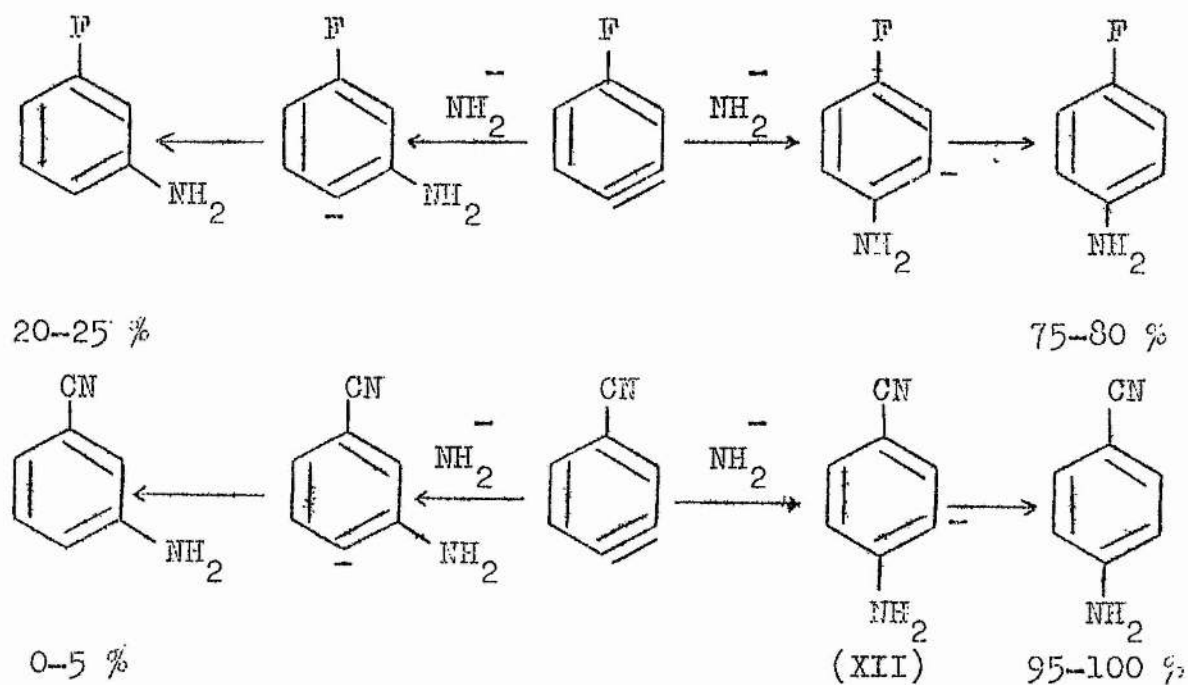
R = CH <sub>3</sub>	55	45%
R = OCH <sub>3</sub> (-I, + M)	0-5	95-100%

The orientation of addition of a nucleophile to benzyne substituted at position three is determined primarily by the inductive (I) effect of the group R on the transition state, electron attracting substituents directing attack to position one. Conjugative (M) effects are of secondary

importance.



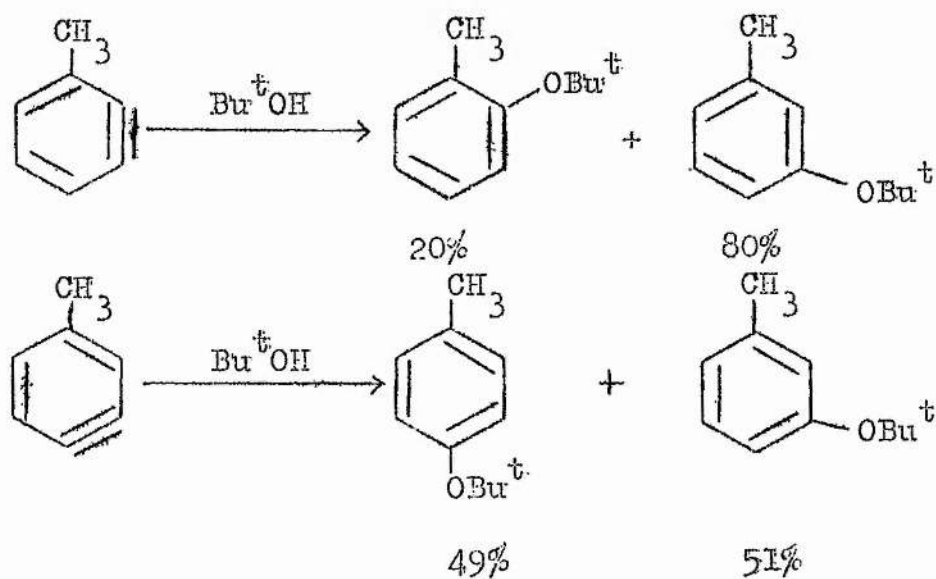
The inductive effect of a substituent at position four, being farther from the dehydro bond, has less influence on the orientation of addition: conjugative effects now assume comparative importance. This last point is demonstrated by the aminations of p-bromofluorobenzene and p-bromobenzonitrile.



The para-to-meta ratio of the aminobenzonitrile surpasses considerably that of the fluoroaniline. Since the fluorine atom and the cyano group have similar electron attracting inductive effects, the marked preference for transition state(XII) in the amination of p-bromobenzonitrile can not be attributed solely to the inductive effect of the cyano group, but must also be due to conjugation between the amino and cyano groups.

Non-cyclic addition to a benzyne carrying a bulky substituent at position three might be expected to exhibit marked steric influences, the attacking entity being very largely directed to position one. Little information is available to support this hypothesis, although the results of work by Cadogan, Hall and Sharp<sup>56</sup> suggest that steric effects may influence the addition of a bulky reagent to benzyne with a (non-bulky) substituent at position three,

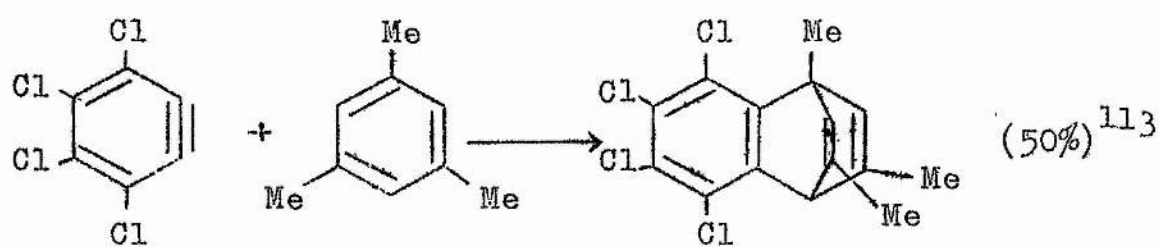
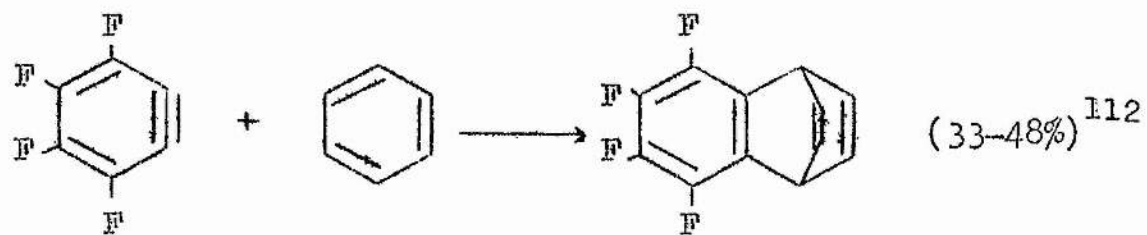
e.g.





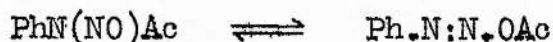
4-Methylbenzyne, formed from p-bromotoluene and potassium t-butoxide, gives 51% m-tolyl t-butyl ether - a rather smaller proportion of meta-isomer than is obtained from the addition of ammonia to this aryne (60%).<sup>109</sup> The corresponding reactions of 3-methylbenzyne yield only 20% o-tolyl t-butyl ether, in contrast to 55% o-toluidine,<sup>109</sup> possibly as a result of steric inhibition of attack at position two by the voluminous nucleophile.

Several factors - their high reactivity, the complexity of many of their reactions, and the impossibility of making direct competitive measurements - militate against an accurate assessment of the effect of substituents on the reactivity of arynes. Zieger and Wittig<sup>110</sup> have looked for reduced reactivity in benzyne substituted at positions three ( $\text{NMe}_2$ ; + M) and six ( $\text{SO}_2\text{Ph}$ ; -I), but their results are not conclusive. Consideration of the behaviour of simple dienophiles might suggest that any reduction of the electron density in an aryne intermediate will result in a corresponding increase in its dienophilicity.<sup>111</sup> The reactivity of tri- and tetra-halobenzyne in Diels-Alder addition to such unreactive dienes as benzene and mesitylene shows this to be the case, e.g.



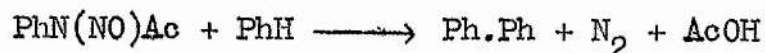
ACYLARYLNITROSAMINES

In 1876, Fischer<sup>114</sup> reported the formation of an unstable yellow solid when nitrous fumes were passed into a cold solution of acetanilide in glacial acetic acid. This material appeared to be N-nitrosoacetanilide; and the following year he prepared other acylarylnitrosamines in a similar manner.<sup>115</sup> An alternative route to these compounds was discovered by von Pechmann,<sup>116</sup> who obtained p-methyl-N-nitrosobenzanilide by treatment of an alkaline solution of p-toluenediazonium chloride with benzoyl chloride. Acetylation of benzenediazonium salts in alkaline solution gave a product identical to that obtained from acetanilide by Fischer's method of nitrosation.<sup>117</sup> tautomerism between benzenediazoacetate and N-nitrosoacetanilide was suggested:<sup>117,118</sup>

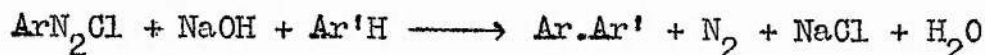


Kühling<sup>119</sup> studied the reactions between dry sodium arenediazotates and aromatic compounds in the presence of acetyl chloride or acetic acid. From the sodium salt of diazotised p-nitroaniline and benzene he obtained 4-nitrobiphenyl, while with toluene a product since shown to be 2-methyl-4'-nitrobiphenyl<sup>120</sup> resulted. Substitution of nitrobenzene for benzene yielded both 2,4'- and 4,4'-dinitrobiphenyls. Bamberger<sup>121</sup> used this reaction, with

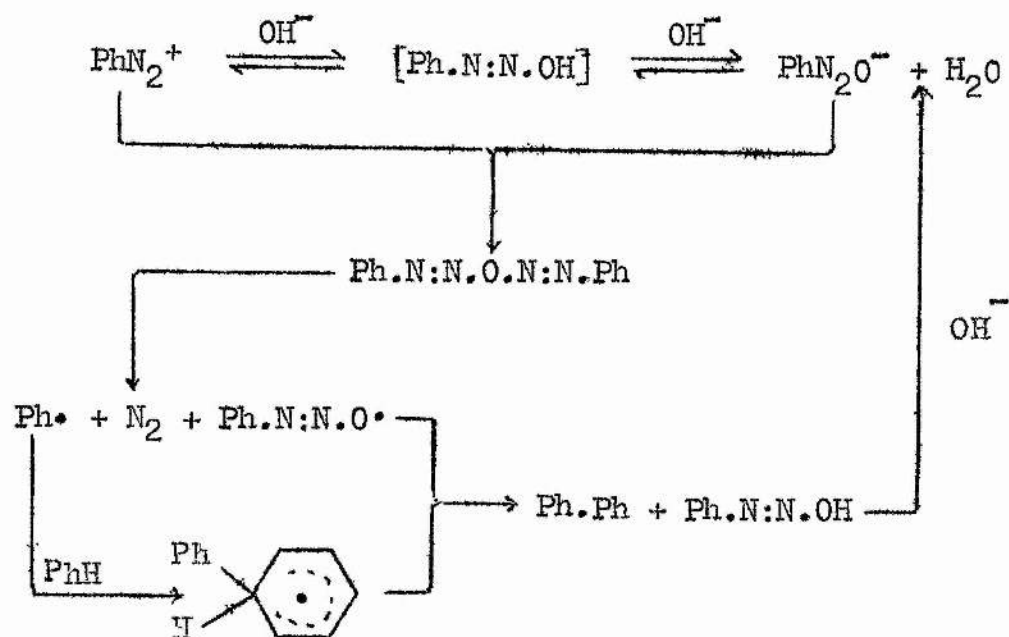
slight modifications, and later showed that the reaction of N-nitrosoacetanilide with benzene gave biphenyl:<sup>6</sup>



The early work of Kühling and Bamberger was developed by Gomberg and his colleagues<sup>122</sup> as a method for the synthesis of biaryls. In this heterogeneous reaction, an aqueous solution of the appropriate diazonium salt, in contact with the aromatic substrate (or a solution of the substrate in a suitable solvent<sup>123</sup>), is treated with sodium hydroxide or sodium acetate, e.g.



As a preparative method, the Gomberg reaction suffers from the formation of large amounts of intractable tar, and frequently, a poor yield of the required biaryl. In 1964 Rüchardt and Merz<sup>124</sup> postulated a mechanism in which the aryl radicals were formed by the homolysis of an intermediate diazoanhydride, e.g.



This scheme has many features in common with that proposed by Rüchardt and Freudenberg<sup>125</sup> for the decomposition of acylarylnitrosamines, which is discussed later.

Bamberger's preparation of biphenyl inspired Grieve and Hey,<sup>7</sup> in 1934, to develop the use of acylarylnitrosamines in syntheses of biaryls. Dry solutions of N-nitrosoacetanilide in a variety of monosubstituted-benzene solvents were allowed to react at room temperature yielding biphenyls substituted at the two- or four- position, irrespective of the nature of the substituent. When m-xylene was used as solvent 2,4-dimethylbiphenyl resulted, while with o-nitrotoluene the product was 3-methyl-4-nitrobiphenyl, no 4-methyl-3-nitro-

biphenyl being detected. The Gomberg reaction gave results very similar to those obtained with acylarylnitrosamines, and further, when a mixture of toluene and nitrobenzene was phenylated, the yield of nitrobiphenyl exceeded that of methylbiphenyl. Sufficient information relating to aromatic substitution was available at that time to indicate the incompatibility of such results with a mechanism involving attack on the substrate by cationic (electrophilic) or anionic (nucleophilic) species. Grieve and Hey<sup>7</sup> therefore suggested that the reactive entity in these reactions was an electrically-neutral free phenyl radical. They argued that the absence of biphenyl from the products of decomposition of N-nitrosoacetanilide in aromatic solvents (other than benzene) did not constitute evidence against the intermediacy of phenyl radicals, but rather indicated that in solution, the radicals were too short-lived to dimerise. The appearance of biphenyl in methanol was supposed to be related to the formation of formaldehyde:

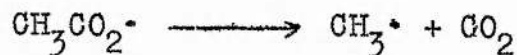


Subsequent experiments appeared to confirm that N-nitrosoacetanilide would react with a substituted benzene to yield a biphenyl substituted at the four- and/or two-

position.<sup>28,126</sup> Comparable results were obtained with dibenzoyl peroxide and phenylazotriphenylmethane - other probable sources of phenyl radical - except that decomposition of the peroxide in ethyl benzoate afforded a small amount of ethyl biphenyl-3-carboxylate in addition to the expected two- and four- isomers.<sup>28</sup> Careful re-examination of the products from the reaction of N-nitrosoacetanilide with ethyl benzoate revealed that there, also, some substitution at the meta-position had occurred.<sup>28</sup> These were the first reported instances of all three isomers being isolated from the arylation of a monosubstituted benzene, although later experiments, with improved techniques, were to reveal that in general all possible positional isomers will be formed to some extent. Williams<sup>127</sup> has discussed these results in detail, concluding that homolytic arylation of an aromatic compound results in an isomer distribution markedly different from that found in ionic substitution, and largely independent of the source of aryl radicals. Huisgen and Grashey<sup>128</sup> have confirmed that arylation differs from 'normal' aromatic substitution not only in the position at which attack occurs, but also in the selectivity of the radical for different substrates. When N-nitrosoacetanilide is allowed to decompose in an equimolar mixture of pyridine and benzene, equal yields of biphenyl and phenylpyridine are obtained. Replacement of benzene by a

monosubstituted benzene  $C_6H_5R$  ( $R = Cl, Br, CH_3, NO_2, CN, OCH_3, Ph$ ) results in a yield of biaryl one-to-three times that of phenylpyridine, irrespective of the electron withdrawing or releasing capacity of the substituent.

In 1937, Waters<sup>129</sup> conducted experiments designed to demonstrate the formation of acetoxy radicals in the decomposition of N-nitrosoacetanilide. When a solution of the nitrosamide in carbon tetrachloride or carbon disulphide was left in the presence of a metal such as zinc, iron, copper or lead, together with an excess of calcium carbonate to remove any acetic acid that might be produced, a metal salt, thought to be the acetate, was formed. The evolution of carbon dioxide observed when N-nitrosoacetanilide was allowed to decompose in acetic anhydride or carbon disulphide was attributed to the breakdown of acetoxy radicals:

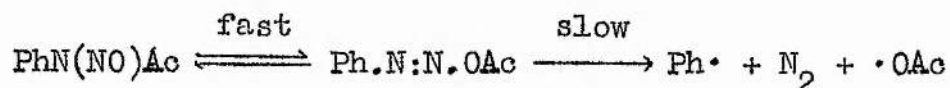


With solvents such as hexane and ether, benzene was formed, but in a halogen-containing solvent, a halobenzene resulted.

Hey and his co-workers<sup>7,130</sup> investigated the kinetics of the decomposition of N-nitrosoacetanilide in solution at 20°, measuring the rate of nitrogen evolution in a wide variety of aliphatic and aromatic solvents. With the exception of acetic acid, first-order kinetics were



invariably observed, and the rate constant was found to vary little, indicating insensitivity of the decomposition to the nature of the solvent. Consequently a reaction scheme was proposed in which the rate-determining step was homolysis of benzenediazoacetate formed by rearrangement of the nitrosamide:<sup>130</sup>



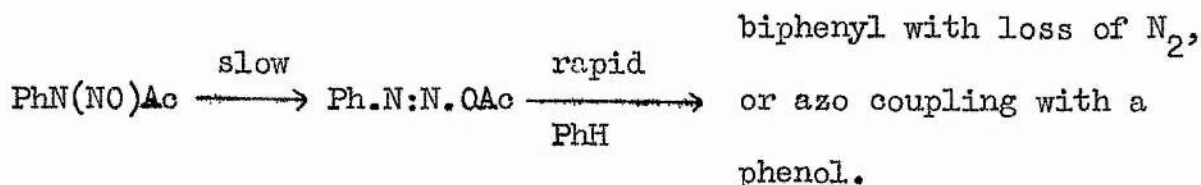
Measurement of the temperature variation of the rate constant for the decomposition of N-nitrosoacetanilide in benzene allowed a value of 22 kcal. per mole to be assigned to the Arrhenius energy of activation.<sup>130</sup>

Several workers presented as evidence for the homolytic nature of acylarylnitrosamine breakdowns the ability of these compounds to initiate polymerisation of vinyl monomers such as styrene, methyl methacrylate and acrylonitrile.<sup>131,132</sup> When the aryl group of the nitrosamide contained bromine, a halogen-containing polymer resulted; but it was noted that bromine incorporation into the polymer was much less marked when the halogen substituent was in the acyl group.<sup>131</sup>

The participation of free radicals both in the Gomberg reaction and in acylarylnitrosamine decompositions was questioned by Hodgson<sup>133</sup> in 1948, on the grounds that all

the observed facts could be accounted for by postulating purely ionic mechanisms for the reactions. A detailed reply was published by Hey and Waters<sup>134</sup> in which they vigorously defended their theories of homolytic aromatic substitution.

In 1949, Huisgen and Horeld<sup>135</sup> discovered that N-nitrosacetanilide, in each of a variety of solvents at 25°, coupled with a phenol such as 2-naphthol at the same rate as nitrogen was eliminated in the absence of phenol. They reasoned that the intermediate common to both these reactions must be the covalent diazoacetate, and that the mechanism that had been proposed earlier by Butterworth and Hey<sup>130</sup> in which rapid rearrangement of N-nitrosoacetanilide to benzenediazoacetate had been followed by slow homolysis - was tenable no longer. Huisgen and Horeld<sup>135</sup> therefore suggested a scheme in which rearrangement was the rate-determining step:

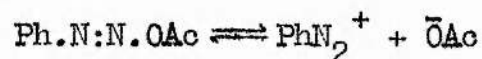


Their kinetic measurements were in general agreement with those that had been produced earlier by Hey and his colleagues,<sup>7,130</sup> indicating insensitivity of the first-order

rate constant for N-nitrosoacetanilide either decomposing with elimination of nitrogen or coupling with a phenol, to changes in the nature of the solvent; except that in acetic acid, nitrogen was evolved only after an induction period, and then more slowly than in any other solvent, although the rate of azo coupling was similar to that in other solvents.

Thorough investigation by a number of workers confirmed the anomalous behaviour of N-nitrosoacetanilide in acetic acid. Two factors were thought to be largely responsible:<sup>135,136,137</sup>

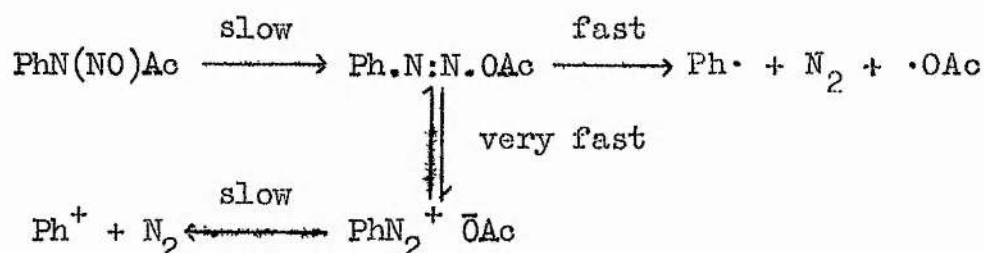
- i) Denitrosation of N-nitrosoacetanilide in a bimolecular reaction with acetic acid.
- ii) Heterolytic fission of the covalent diazoacetate in an equilibrium process,



which would favour the ions in acetic acid, but would be unimportant in other organic solvents. The concentration of diazoacetate would thus be reduced, there being present mainly diazonium salt, which would decompose slowly to yield molecular nitrogen and phenyl acetate.

Similar behaviour was observed with N-nitrosoacetanilide in other carboxylic acids, although acetic anhydride acted as a 'normal' solvent.<sup>137</sup>

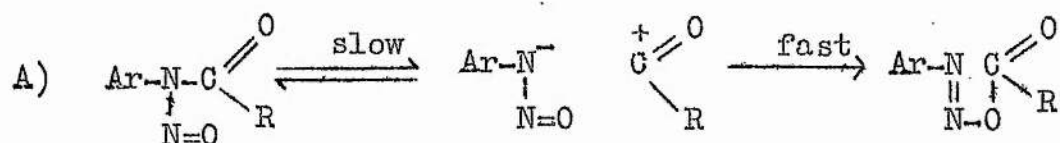
De Tar,<sup>138</sup> in 1951, investigated the decomposition of N-nitrosoacetanilide in methanol, both in the presence and absence of certain added substances. In pure methanol, and in methanol containing sodium acetate, benzene and formaldehyde were formed, as had been reported earlier by Grieve and Hey.<sup>7</sup> With sulphuric acid as additive, however, anisole was the major product, little benzene being detected. De Tar concluded that in neutral or basic solution, phenyl radicals were produced which could abstract hydrogen from the solvent to give the observed products, but anisole must have resulted from the formation of carbonium ions in acid solution. He proposed a scheme for N-nitrosoacetanilide which allowed for azo coupling via the diazonium cation (rather than through the diazoacetate) even in a non-polar solvent, and in which the course of decomposition would be governed by the nature of the solvent:

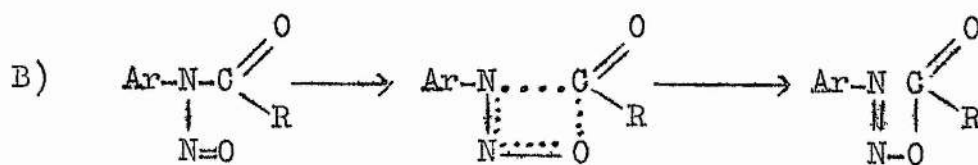


De Tar<sup>138</sup> also measured the yield of carbon dioxide from the decomposition of N-nitrosoacetanilide in a number of solvents, and found it to be appreciable only in acetic anhydride (20%).

Huisgen and Nakaten<sup>139</sup> challenged the assertion that the formaldehyde which was formed in the decomposition of N-nitrosoacetanilide in methanol arose from oxidation of the solvent by phenyl radicals.<sup>7,138</sup> When o-methyl-N-nitrosoacetanilide was dissolved in chloroform, indazole resulted in almost quantitative yield; but in ethanol both N-nitrosoacetanilide and o-methyl-N-nitrosoacetanilide gave high yields of acetaldehyde. In the latter case little indazole was formed, indicating that oxidation must have been achieved at the expense of cyclisation by some species still containing nitrogen and not, therefore, a phenyl radical.

The rate-determining step for acylarylnitrosamines undergoing either azo coupling or nitrogen-eliminating decomposition having been established to be rearrangement to a diazoester,<sup>135</sup> attention was focused on the mechanism by which the acyl group migrated from nitrogen to oxygen. Elucidation of this problem resulted from the simultaneous but independent investigations of the groups of Hey<sup>137</sup> and Huisgen,<sup>139,140</sup> both of whom considered two possible schemes:





Effect of Substituents in the Aryl Group. -- Hey<sup>137</sup>

investigated the kinetics of the decomposition in benzene of a number of meta- and para-substituted derivatives of N-nitrosoacetanilide. Although the substituents had very different electronic properties, similar values of the first-order rate constant were found for all the nitrosamides at 25°, and in addition, for the para-compounds, the value of the Arrhenius energy of activation was found to be practically invariant. In mechanism A electron withdrawing substituents would facilitate heterolysis and hence rearrangement, contrary to experimental observations. For B, however, it would be possible for any assistance given to the cleavage of the nitrogen-carbon bond to be offset by an adverse effect on the polarisation of the nitroso group. Huisgen<sup>140b</sup> confirmed Hey's measurements, and in addition discovered that an ortho-substituent, irrespective of its electronic character, reduced slightly the rate of rearrangement. A steric effect was suggested, by way of which an ortho-substituent would impair the ability of the aryl group to attain coplanarity with - and hence provide resonance stabilisation of - the

four membered ring in the intermediate in mechanism B.

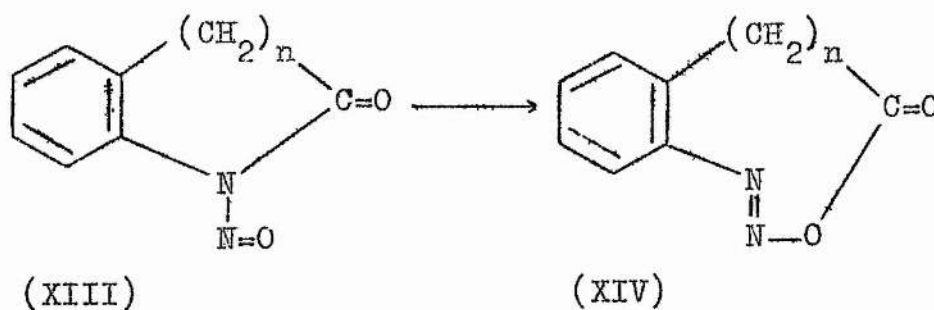
Effect of Varying the Acyl Group. - Both Hey<sup>137</sup> and Huisgen<sup>140b</sup> observed in a series of acylphenylnitrosamines a small increase in the first-order rate constant as the size of the acyl group was increased from formyl to isopropanoyl. Although the gradation was in a direction opposite to that expected for simple SN-2 attack on the carbonyl-carbon of the acyl group, they reasoned that the smallness of the variation was incompatible with the heterolytic mechanism A, and was better reconciled to B, which in any case could not be considered a perfect analogy to simple SN-2. Huisgen arrived at the same conclusion, suggesting that a voluminous acyl moiety assisted the molecule to attain the configuration required for nucleophilic attack by the carbonyl-carbon on the nitroso-oxygen atom. Heyns and Bebenburg<sup>141</sup> disputed that the results could be reconciled with an exclusively non-polar mechanism.

Solvent Effects and Salt Effects. - The rate constant for the decomposition of N-nitrosoacetanilide in ethanol containing varying proportions of water, and in ethanol containing lithium chloride, was found by Hey<sup>137</sup> to be the same as that for the reaction in anhydrous ethanol. He thought the absence of solvent effects and salt effects discriminated strongly against heterolytic mechanism A.



Intermolecular Deacylation. - Formation of the cyclic intermediate postulated in B would require deacylation by intramolecular attack of the weakly basic nitroso-oxygen atom on the acyl-carbon. Huisgen<sup>140a</sup> and Hey<sup>137</sup> reasoned that introduction of a strong nucleophile to the system should result in rapid intermolecular deacylation, if mechanism B were operative. When piperidine was added to a solution of N-nitrosoacetanilide in benzene, a sharp increase was observed in the rate of nitrogen evolution, which no longer followed first-order kinetics, but depended on the concentration of base.

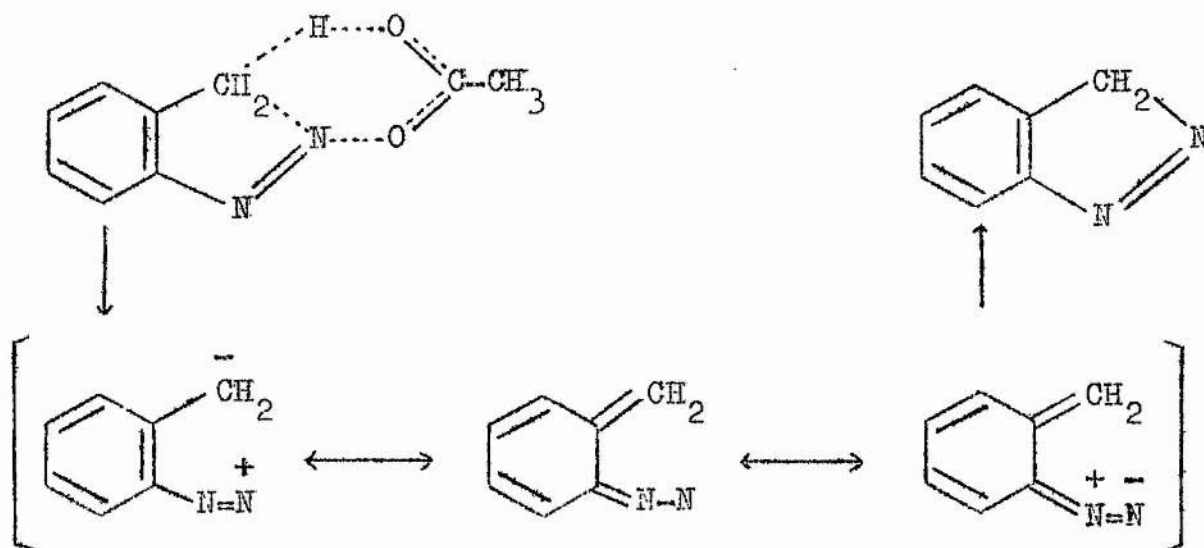
Configuration of the Diazoester. - The diazoester, if formed through a cyclic mechanism such as B, would have the trans-configuration. Huisgen's experiments<sup>140c,d</sup> on the rearrangement of N-nitrosobenzolactams (XIII) to cyclic diazoesters (XIV) demonstrated convincingly that such was the case.



Only when  $n$  was equal to, or greater than, three did rearrangement occur, consistent with the product (XIV)



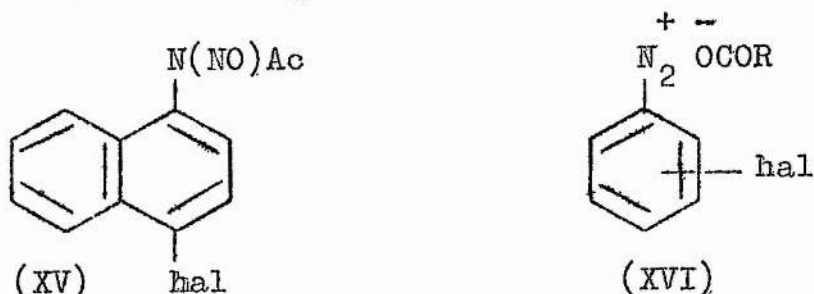
having the trans-configuration, when a nine membered ring would be the smallest unstrained structure. The formation of indazole by o-methyl-N-nitrosoacetanilide was also thought to point to a trans-diazooacetate.<sup>140e</sup>



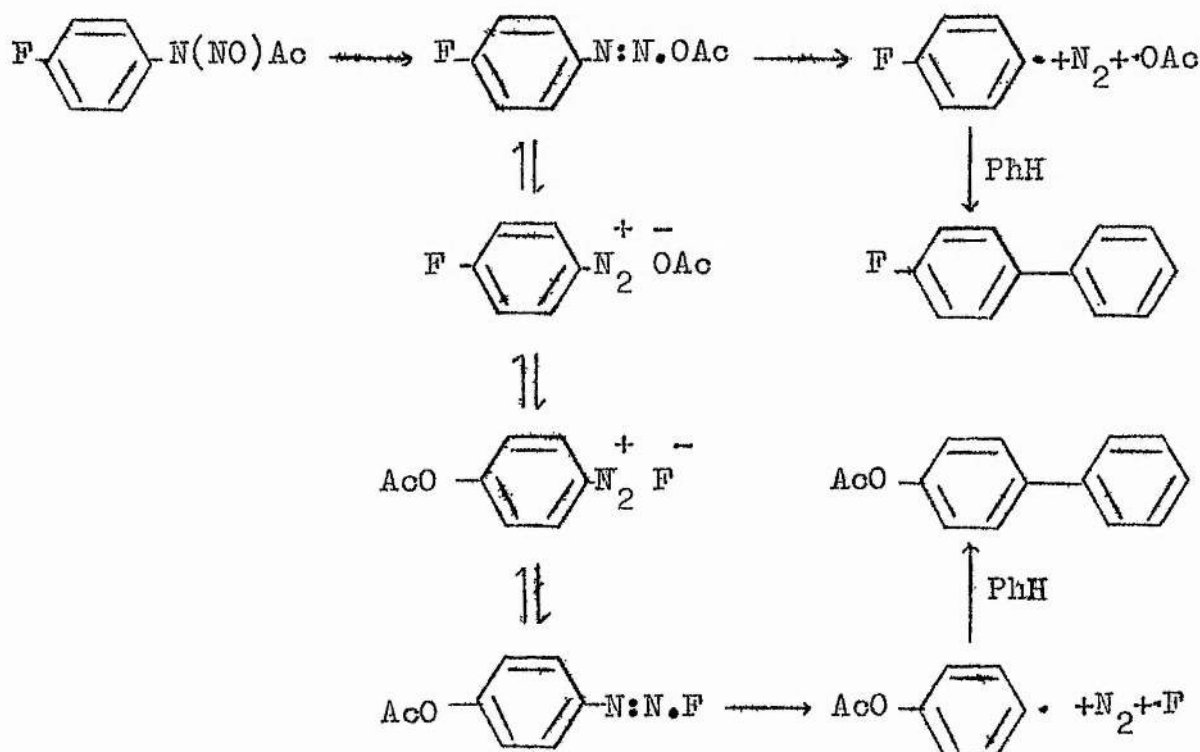
In 1960, Suschitzky and his collaborators<sup>142,143</sup> initiated an investigation into heterolytic processes occurring during the decomposition of acylarylnitrosamines in non-polar solvents. The decompositions of o- and p-fluoro-N-nitroso-acetanilides and -benzanilides in benzene yielded in addition to the expected 2- and 4-fluorobiphenyls, comparable amounts of 2- and 4-acyloxybiphenyls.<sup>142b</sup> Fluorine meta to the nitrosamide function, and any other halogen in the ortho- or para- position, was not displaced,

although evidence was obtained for the substitution of chlorine and bromine as well as fluorine in the decompositions of 4-halo-N-acetyl-N-nitroso-1-naphthylamines (XV).<sup>142a</sup>

These results were thought to indicate the formation of

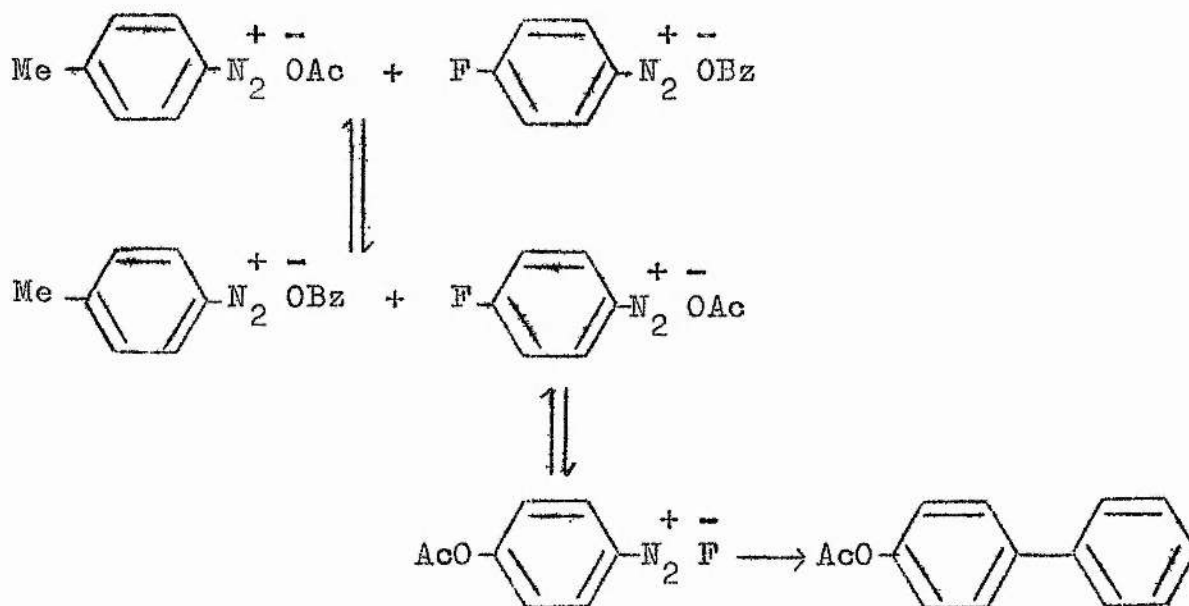


ion pairs (XVI) from halogen-substituted N-nitrosoacylanilides, with subsequent displacement by the nucleophilic anion of the halogen in the activated o- or p-fluorobenzenediazonium cation; fluorine meta to the diazonium group, being less activated, could not be displaced.<sup>142b</sup>

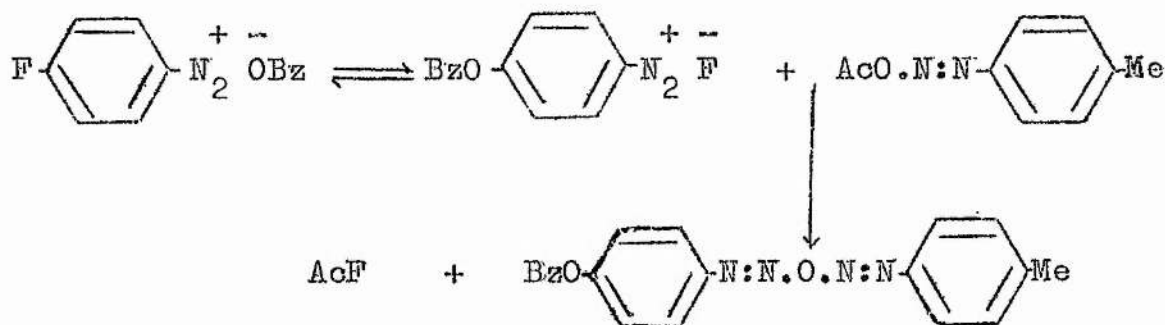


Halogen substituents other than fluorine were supposed to be less labile in the diazonium cation.

In an attempt to establish the generality of ion-pair formation by acylarylnitrosamines, various acetylarylnitrosamines with substituents of differing electronic character (para-H, CH<sub>3</sub>, NO<sub>2</sub>, Cl; meta-CH<sub>3</sub>) were each allowed to decompose in benzene containing p-fluoro-N-nitrosobenzanilide. In every case, the mixed product, 4-acetoxybiphenyl, was isolated, confirming the formation of ion pairs by both nitrosamides, with subsequent exchange of partners,<sup>142a</sup> e.g.



Acetyl fluoride - detected in these reactions - was thought to arise by way of nucleophilic attack of fluoride ion on the diazoacetate:

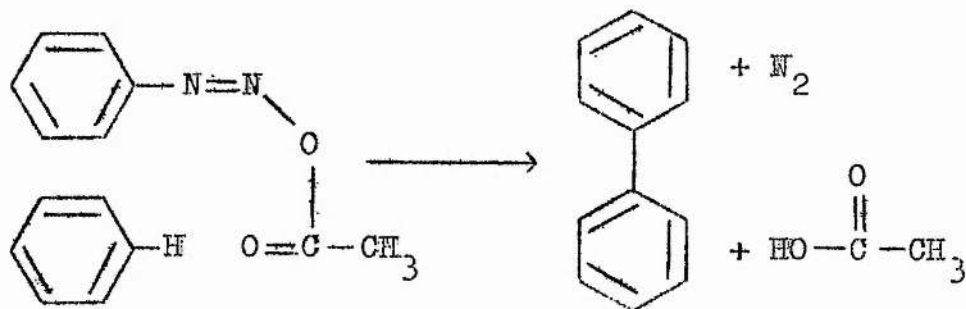


The concomitant diazoanhydride would be able to fragment to give aryl radicals, as had been suggested many years before by Bamberger.<sup>144</sup>

Miles and Suschitzky<sup>142a</sup> concluded that in the reactions of acylaryl nitrosamines, even in non-polar solvents, heterolysis of the covalent diazoester might be important; and they questioned the validity of Huisgen's assertion<sup>135,136,140</sup> that in solvents such as benzene, azo coupling with phenols occurred via the diazoester, preferring to attribute this to the diazo ion pair.

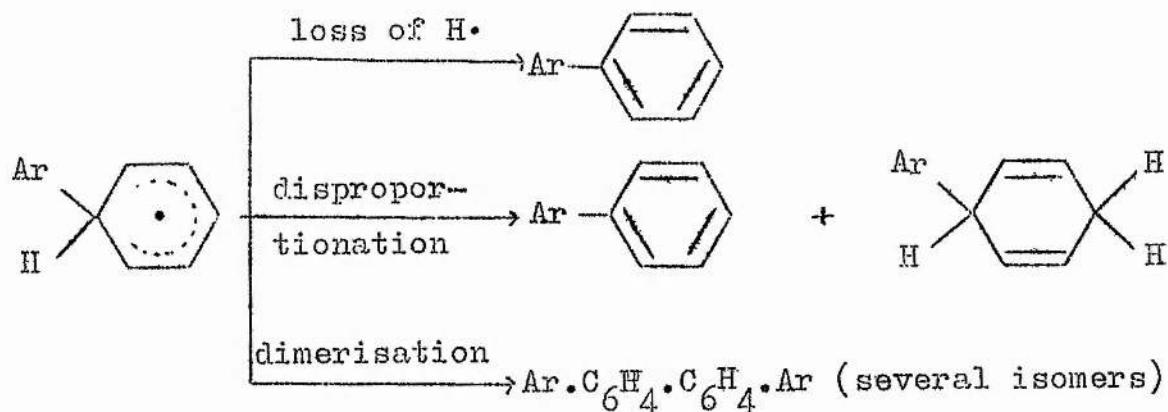
Suschitzky and his colleagues,<sup>142</sup> in common with earlier workers, supposed the high yield of acetic acid formed in the decomposition of N-nitrosoacetanilide in benzene to arise through the intermediacy of acetoxyl radicals. The great instability of the acetoxyl radical, fragmenting to a methyl radical and carbon dioxide, had, however, been established some years earlier;<sup>12,13</sup>

and although Water's (non-quantitative) experiments<sup>129</sup> had shown that N-nitrosoacetanilide could suffer homolysis to acetoxy radicals, no evidence had been presented to suggest that they, or their decomposition products, were formed in the major reaction path; indeed the absence of carbon dioxide in high yield had been noted by several workers.<sup>12,125,135,138</sup> Information such as this, together with the knowledge that a polymer whose formation had been initiated by an acylarylnitrosamine exhibited little acyl group incorporation, had lead Huisgen and Horeld,<sup>135</sup> in 1949, to question the participation of free acetoxy radicals in the decomposition of N-nitrosoacetanilide. They suggested instead that a "krypto-radical" mechanism might be operative, the covalent diazoacetate undergoing homolysis only when a solvent molecule (such as benzene) was suitably positioned for a concerted reaction to occur:



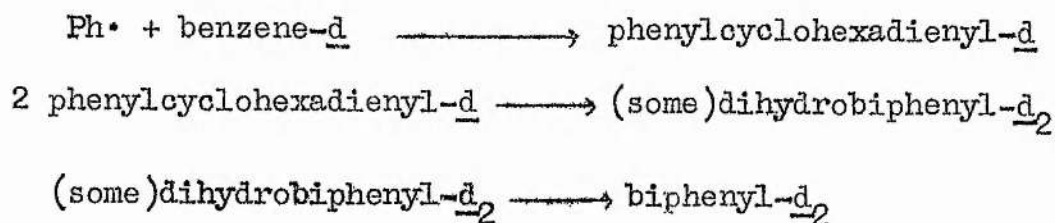
The arylation of benzene with diaryl peroxides has been shown to proceed through an arylcyclohexadienyl radical~

formed by additive attack of an aryl radical on the substrate - which may react in one of three ways:<sup>49,145</sup>



In addition to the required biaryl, dihydrobiaryls and tetrahydroquateraryls will be formed as byproducts.

In 1962, Eliel, Eberhardt and Simamura<sup>146</sup> undertook a careful examination of the products resulting from the decomposition of N-nitrosoacetanilide and of phenylazotriphenylmethane in benzene; in neither case was dihydrobiphenyl detected. They then repeated the reactions in the presence of added dihydrobiphenyl - and recovered it largely unchanged when the decompositions were complete. When dibenzoyl peroxide was allowed to decompose in benzene-d, a small proportion (ca. 0.5%) of the resulting biphenyl contained two deuterium atoms:

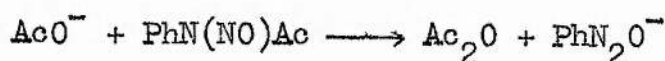


Similar experiments with both p-chloro-N-nitrosoacetanilide and p-chlorophenylazotriphenylmethane yielded appreciably less biphenyl-d<sub>2</sub>. Eliel and his collaborators<sup>146</sup> suggested that the decomposition of N-nitrosoacetanilide (or phenylazotriphenylmethane) in benzene was "diffusion-controlled", the phenyl and acetoxy (or triphenylmethyl) radicals being generated simultaneously, and in juxtaposition. Rapid, synchronous reaction with a benzene molecule by addition and hydrogen abstraction would result in biphenyl and acetic acid (or triphenylmethane). They attributed the contrasting behaviour of dibenzoyl peroxide to the relative stability of the benzoyloxy radicals, which they supposed could diffuse apart before gradually decomposing to truly free phenyl radicals and carbon dioxide. More recent experiments by several workers have shown that not more than a small fraction of the radicals formed in the decomposition of phenylazotriphenylmethane in benzene can be "caged" as had been suggested: but they have also revealed that the absence of dihydrobiphenyl and tetrahydroquaterphenyl may be attributed to the relative stability of the triphenylmethyl radical.<sup>33,147,148</sup>

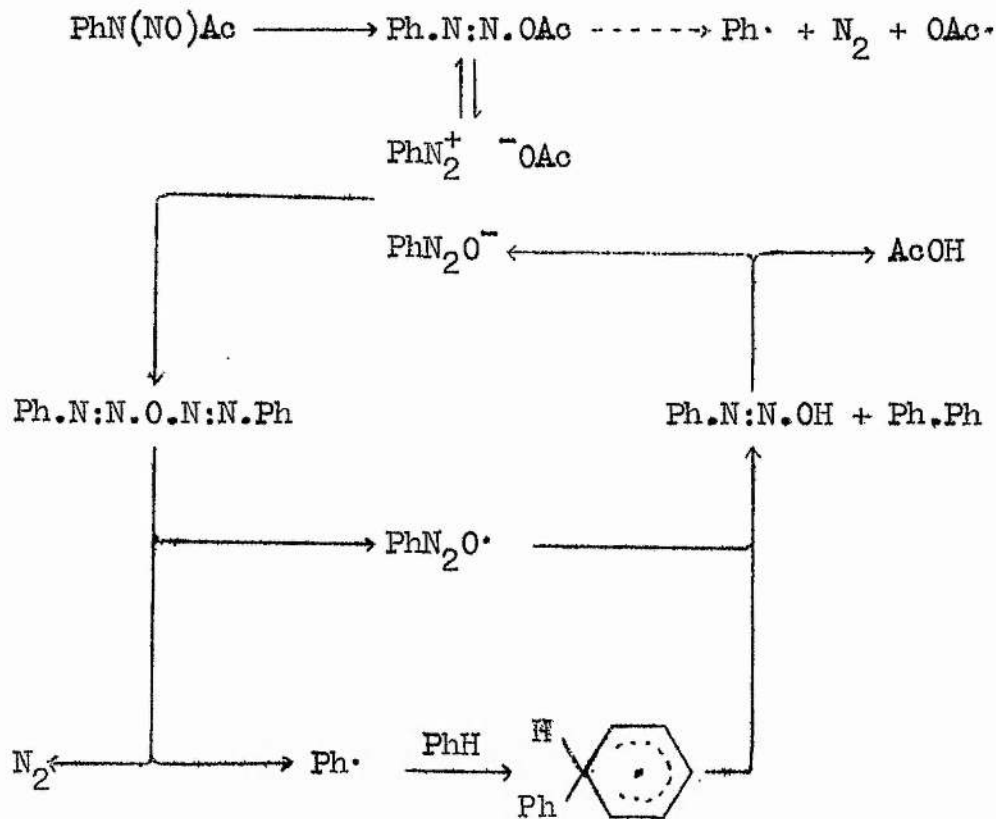
Denney, Gershman and Appelbaum<sup>149</sup> questioned the proposed "cage" mechanism for the decomposition of N-nitrosoacetanilide in benzene when they found that inclusion of a radical interceptor such as styrene suppressed biphenyl.

formation without influencing the elimination of nitrogen. In 1964, Eliel and Saha<sup>150</sup> discovered that the decomposition of N-nitrosoacetanilide in benzene containing iodine in low concentration resulted in a high yield of iodobenzene, indicating the essential freedom of the phenyl radicals formed. The suggestion of a "diffusion-controlled" or "cage" mechanism for the decomposition of acylarylnitrosamines in benzene was withdrawn; leaving no explanation of the absence of products which would result from dimerisation and disproportionation of arylcyclohexadienyl radicals, or of the formation of carboxylic acids (supposedly) from unstable acyloxy radicals.

It was also in 1964 that Rüchardt and Merz<sup>124</sup> proposed a mechanism for the Gomberg reaction in which aryl radicals were formed by the homolysis of a diazoanhydride; and that the same precursor was suggested by Rüchardt and Freudenberg<sup>125</sup> for the radicals formed in the decomposition of acylaryl-nitrosamines in aromatic solvents. Common also to the two reaction schemes was the idea that major products were formed in a chain process, as shown for N-nitrosoacetanilide in benzene. The phenyl diazotate ion, which is regenerated in the chain reaction, was supposed to be formed initially by nucleophilic attack of acetate ion on N-nitrosoacetanilide:



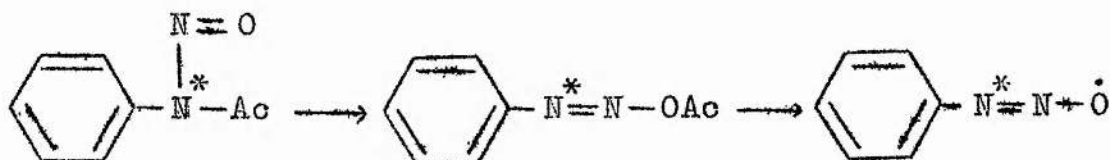




With this mechanism, Rüchardt and Freudenberg<sup>125</sup> claimed that the high yield of acetic acid and the absence of carbon dioxide were readily understood since acetate ions rather than acetoxy radicals were involved; that the anomalous decomposition of N-nitrosoacetanilide in acetic acid could be a consequence either of solvation of acetate ion hindering the initiation process or of displacement of the diazotate-diazonium equilibrium; that the relatively high yield of carbon dioxide from the decomposition in acetic anhydride might be a result of reversal of the initiation

reaction causing a comparatively large amount of the nitrosamide to fragment by simple homolysis; and that clean oxidation of phenylcyclohexadienyl radicals would be expected if the phenyl diazotate radical were sufficiently stable to allow of an appreciable steady-state concentration.

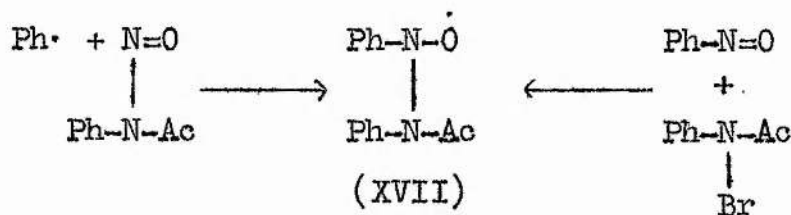
When N-nitrosoacetanilide was allowed to decompose in benzene in the cavity of an e.s.r. spectrometer, the spectrum of a long-lived radical - possibly the postulated diazotate radical - was observed throughout the whole duration of the reaction.<sup>125</sup> Further investigation<sup>151</sup> confirmed that the observed spectrum was that of a radical containing two nitrogen atoms, with spins unequally coupled to the spin of the unpaired electron ( $a = \pm 11.6; \pm 1.7$  gauss). The spectrum of the radical formed from <sup>15</sup>N-nitrosoacetanilide (30.5% isotopically pure) showed less contribution from the smaller coupling constant. By assuming the accepted mechanism for the rearrangement, viz.



it was possible to assign the larger coupling constant to the nitrogen adjacent to oxygen in the diazotate radical. The spectra from p-t-butyl-N-nitrosoacetanilide and p-deutero-N-nitrosoacetanilide suggested an angled

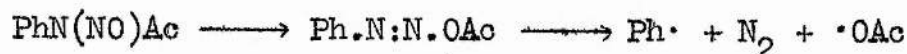
structure for the aryl diazotate radical.

A radical with an e.s.r. spectrum essentially the same as that observed during the decomposition of N-nitrosoacetanilide in benzene was reported by Perkins and his colleagues,<sup>152</sup> in 1967, to be formed in the reaction of nitrosobenzene with N-bromoacetanilide. They considered that the most probable intermediate common to these reactions was the nitroxide radical (XVII),

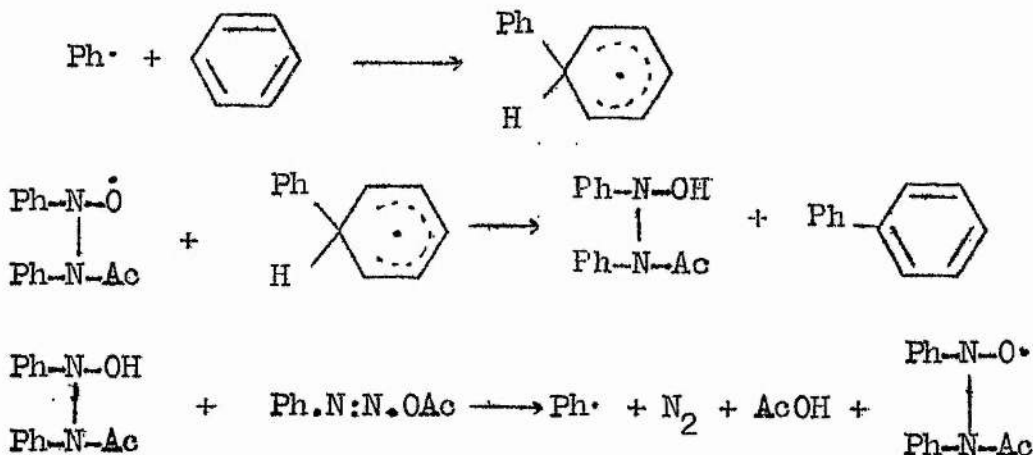


and accordingly proposed a modified scheme for the decomposition of N-nitrosoacetanilide in benzene.

Initiation:

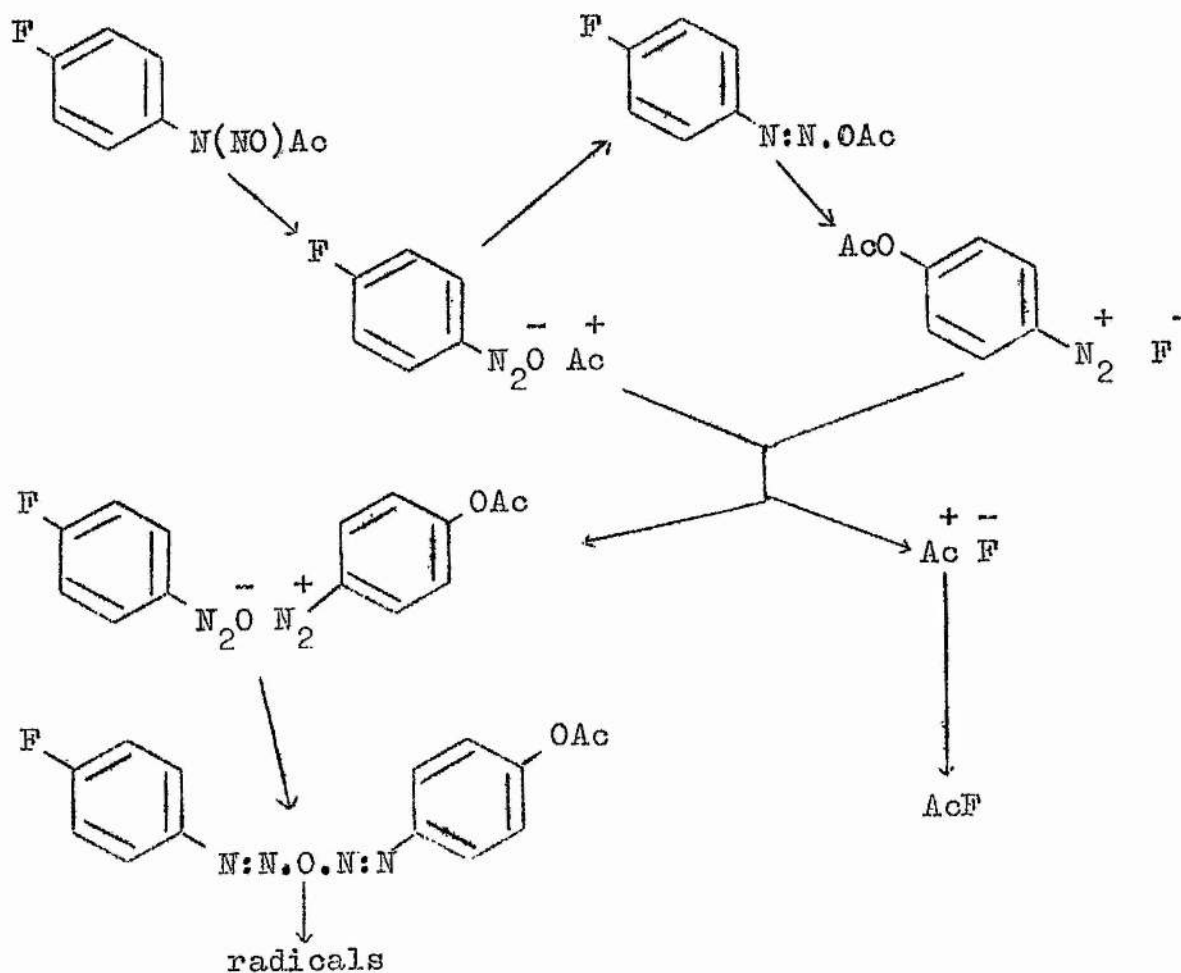


Main product forming sequence:

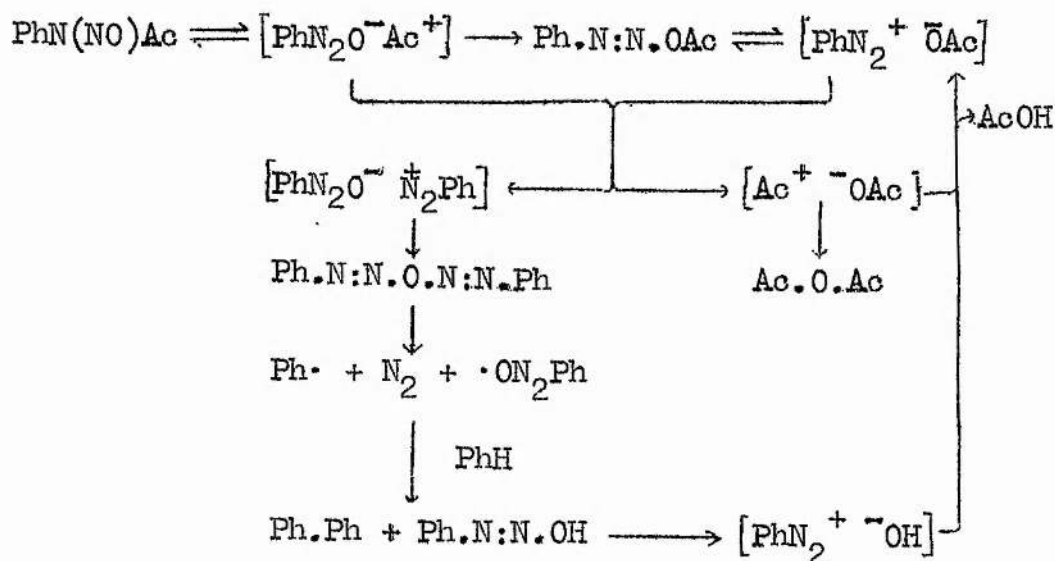


The details of the last reaction were not defined, although it was conceded that more than one stage might be involved.

A different modification of Rüchardt and Freudenberg's scheme was presented by Suschitzky.<sup>143</sup> To rationalise the formation of acetyl fluoride in the decomposition of p-fluoro-N-nitrosoacetanilide in benzene, he suggested that both the nitrosamide and the diazoacetate could suffer heterolysis to an ion pair; that an exchange of ions could then produce new ion pairs; and that ultimately acetyl fluoride and a diazoanhydride would result.



Suschitzky further suggested that spontaneous heterolysis of N-nitrosoacetanilide (in benzene) was a more likely source of phenyl diazotate anion than was the attack of acetate ion on the nitrosamide, as had been proposed by Richardt and Freudenberg. Modified thus the scheme became:

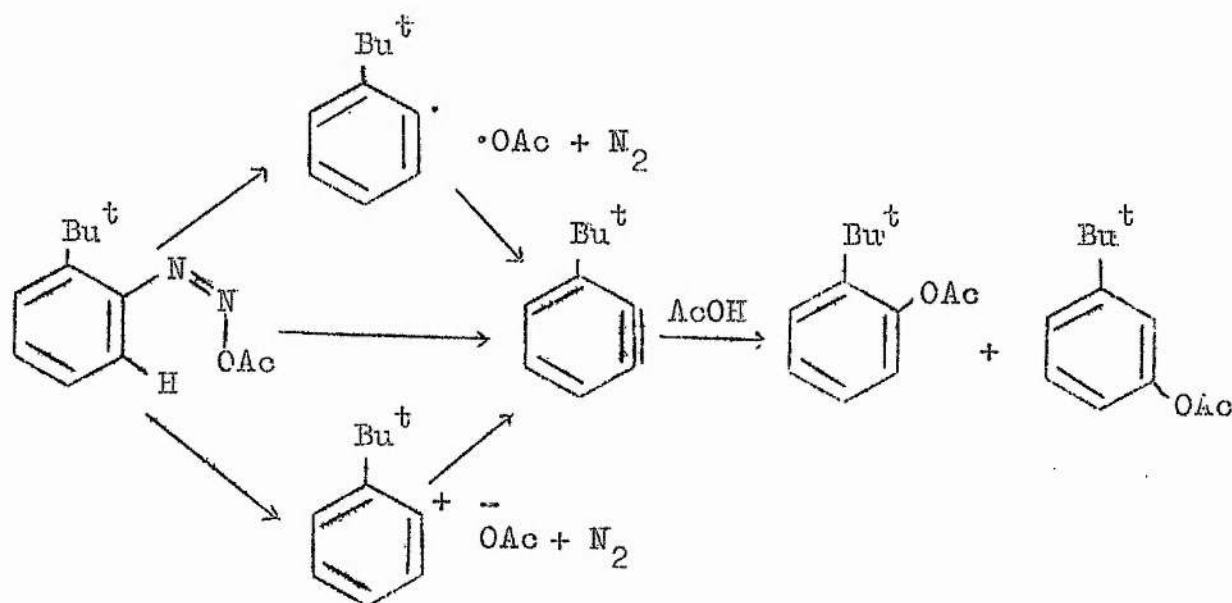


Suschitzky considered that the results obtained earlier by Hey and by Huisgen from their investigations into the mechanism of the rearrangement of N-nitrosoacetanilide could be readily reconciled with his suggestion that the diazoacetate was formed by way of an ion pair.

The basic postulates of Richardt and Freudenberg's theory of the decomposition of N-nitrosoacetanilide in benzene - that acetic acid is formed in an ionic reaction,

and that the presence in the system of a long-lived radical ensures clean oxidation of the phenylcyclohexadienyl radicals, to the exclusion of their dimerisation and disproportionation - remain unchallenged, and permit rationalisation of two of the outstanding features of the reaction. Such ideas do not, however, offer any explanation of the anomalous decomposition of o-t-butyl-N-nitrosoacetanilide. Cadogan, Hey and Williams<sup>153</sup> reported in 1954 that while p-t-butyl-N-nitrosoacetanilide in benzene gave the expected 4-t-butylbiphenyl, the o-isomer yielded a mixture of isomeric t-butylphenyl acetates, with only a trace of the biaryl. The unusual behaviour of this nitrosamide - confirmed by Rondestvedt and Blanchard<sup>154</sup> - was the subject of a more detailed investigation by Cadogan and Hibbert<sup>8</sup> in 1964. They found that the ester mixture (total yield 46%) formed in benzene contained o- and m-t-butylphenyl acetates in the ratio of two to one and that the p-isomer was absent. When the decomposition was repeated in the presence of anthracene, 1-t-butyltritycene (9%) was isolated; and the ester mixture (20%), reduced in total yield, was found to contain relatively more o-t-butylphenyl acetate. Cadogan and Hibbert<sup>8</sup> postulated the participation of 3-t-butylbenzyne, which in the absence of an arynophile could add acetic acid to form the o- and m-esters; but to account for the different composition of the ester mixture

formed in the presence of anthracene, they suggested that some o-t-butylphenyl acetate was formed by a non-aryne mechanism. A scheme was proposed in which o-t-butyl-N-nitrosoacetanilide, because of the bulk of the o-substituent, rearranged to the cis-diazooacetate (rather than the normal trans-) which then underwent concerted decomposition. On the available evidence, they emphasised, it was not possible to discount alternative stepwise pathways to 3-t-butylbenzynes:



Brydon and Cadogan<sup>155</sup> later investigated the decomposition in benzene of a number of o-substituted N-nitrosoacetanilides and found that in all cases (except o-methyl where intramolecular cyclisation occurred) the major product was the biaryl, although o-phenyl-N-nitrosoacetanilide gave 2- and 3-acetoxylbiphenyls (6.3 and 4.5%) as well as o-terphenyl (21%).

PROGRAMME OF RESEARCH

Of all the simple acetylnitrosamines investigated before 1965, only o-t-butyl-N-nitrosoacetanilide gave a major decomposition-product in benzene whose formation could not be rationalised in terms of free-radical or diazonium-cation intermediacy, but rather required participation by an aryne. A study of acetylnitrosamines with o-substituents comparable in size with the t-butyl group, and of aromatic molecules with more than one N-nitrosoacetamido function, each having an adjacent t-butyl group, might prove to be not only interesting and of possible synthetic application, but also valuable in understanding the anomalous behaviour of o-t-butyl-N-nitrosoacetanilide. No sooner had this work been started than its basic premise -- the uniqueness of aryne participation in the decomposition of o-t-butyl-N-nitrosoacetanilide -- had to be critically examined following Brydon and Cadogan's discovery<sup>155</sup> that N-nitrosoacetanilide forms the 'benzyne adduct', 1,2,3,4-tetraphenylnaphthalene, with 2,3,4,5-tetraphenylcyclopentadienone. It therefore became necessary to establish more clearly the differences between the behaviour of o-t-butyl-N-nitrosoacetanilide and its m- and p- isomers, as well as other acetylnitrosamines in general.



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Symbols and Abbreviations

The abbreviations that appear in this thesis are those in common usage. In addition, the following symbols are used:

J	spin-spin coupling constant
s	singlet
d	doublet
sh	shoulder
m/100m	moles of product per 100 moles of starting material
M	molecular weight
m/e	mass/charge ratio
N	normality
R <sub>f</sub>	ratio of distance moved by the substance to the distance moved by the solvent front

EXPERIMENTAL

Gas-Liquid Chromatography. - Three instruments were used for analytical investigations: a Perkin-Elmer F.11 chromatograph, with a flame-ionisation detector, using 2m. x 2.2 mm. i.d. packed columns or 50 m. x 0.25 mm. i.d. capillary columns; a Varian Aerograph 1520B chromatograph, with a flame-ionisation detector, using 2 m. x 2.2 mm. i.d. packed columns; a Griffin and George D.6 gas-density balance chromatograph, using 2 m. x 5.0 mm. i.d. packed columns. Quantitative measurements were made using the D.6 instrument, the internal-standard technique being that described by Cadogan and Sadler.<sup>157</sup> All standards were purified before use. Preparative g.l.c. usually made use of a Pye Series 105, Model 15, chromatograph, or occasionally, as indicated, an Aerograph A.700. In all cases the carrier gas was nitrogen, the flow rates and split ratios being as recommended by the manufacturers. The following stationary phases, supported on 100-120 mesh celite or silocel, were employed: Carbowax 20M (CAR), neopentylglycol succinate (NPGS), polyethyleneglycol adipate (PEGA), 1,4-butanediol succinate polyester (BDS), fluorosilicone oil (QF-1), silicone oil (SIL) and apiezon L grease (APL).

Column Chromatography. - Alumina was Spence and Sons, Grade H, 100-200 mesh (Brockmann activity = 2) or occasionally,

as indicated, Hopkin and Williams 'Camag' (Brockmann activity = 1). Silica gel was Whatman Chromedia SG31.

Thin-Layer Chromatography. - Chromatograms were obtained on 0.3 mm. or 1.0 mm. (preparative) layers of alumina (Merck, Aluminium Oxide G) or silica gel (Macherey, Nagel and Co., Silica Gel G). Components in the developed chromatogram were detected by their fluorescence in ultraviolet light, or by their reaction with iodine.

Proton Magnetic Resonance Spectroscopy. - A Perkin-Elmer Model R-10 Nuclear Magnetic Resonance Spectrometer, operating at a frequency of 60 Mc./sec. and a probe temperature of 35.5° was used. Chemical shifts are recorded as tau ( $\tau$ ) values in parts per million, tetramethylsilane ( $\tau$ 10.0) being the internal reference. Spectra were determined on 10-15% w/v solutions, or as indicated.

Infrared Spectroscopy. - Liquid samples were examined as thin films; solids as melts or Nujol mulls. Solution spectra were obtained using matched cells (path length indicated) with silver chloride or sodium chloride windows. Perkin-Elmer Model 237 or 257 Spectrophotometers were most commonly used; occasional spectra were recorded on Grubb Parsons Type G.S.2A or Perkin-Elmer Model 137 Spectrophotometers.

Ultraviolet Spectroscopy. - A matched pair of 1 cm. silica cells was used in a Unicam S.P.800 Ultraviolet



### Spectrophotometer.

Mass Spectroscopy.-- Mass spectra were obtained using an Associated Electrical Industries MS9 mass spectrometer, by courtesy of British Petroleum Company Limited, or occasionally, an Associated Electrical Industries MS12 spectrometer, by courtesy of Professor Lord Tedder, University of Dundee. Calculated values of mass-spectral functions are due to Beynon.<sup>200</sup>

Spinning-Band Column Distillations.-- These were performed with a Büchi Drehbandkolonne Type AG unit, the band being of stainless steel. A reflux ratio of 30:1 and a distillation rate of approximately 1 ml. per hour were employed.

Melting Points.-- The melting points of all new compounds were determined on a Kofler hot-stage apparatus.

Photochemical Reactions.-- A Hanovia 100 watt Medium Pressure Mercury Arc Tube - No. 12771/1 in a water-cooled quartz envelope was surrounded by the reaction mixture contained in a 100 ml. capacity Pyrex reaction vessel.

Elemental Analyses.-- Microanalyses were performed by Bernhardt, Mulheim, Germany, by Weiler and Strauss, Oxford, and by Mr. J. Bews, University of St. Andrews.

Solvents.-- Dimethyl sulfoxide was dried over magnesium sulphate, then over calcium hydride, and distilled from calcium hydride in an atmosphere of nitrogen (b.p. 86-8°/20 mm.). Tetrahydrofuran was passed down an alumina column and

distilled from lithium aluminium hydride. Nitromethane and dimethylformamide were distilled and dried over molecular sieve. trans-1,2-Dichloroethylene was dried over calcium sulphate and fractionally distilled, b.p.  $48.5^{\circ}$ . Acetonitrile was distilled from phosphorus pentoxide. Super-dry ethanol was prepared as described by Vogel (Method 1).<sup>158</sup> Benzene- $d_6$  (Ciba, >99 atom % D) was dried over sodium wire. Common solvents were purified by standard procedures. Petroleum refers to the fraction b.p.  $40-60^{\circ}$ ; decalin was a mixture of cis and trans isomers.

Reagents.- Benzyl chloride (b.p.  $76^{\circ}/20$  mm.) and 1-bromobutane were distilled from phosphorus pentoxide. *t*-Butylbenzene was dried over sodium wire and distilled (b.p.  $60^{\circ}/15$  mm.), and its purity checked by g.l.c. Thionyl chloride (100 g.) was distilled from quinoline (20 g.) and the fraction b.p.  $75-7^{\circ}$  redistilled from raw linseed oil (40 g.) to give a colourless product, b.p.  $75-7^{\circ}$ . Triethyl phosphite (Albright and Wilson) was allowed to stand over sodium wire until no further reaction occurred, and was then distilled from sodium in an atmosphere of nitrogen, the fraction b.p.  $59-61^{\circ}/23$  mm. being retained. Cadmium chloride was dried in air at  $120^{\circ}$ . Iron powder (B.D.H. Hydrogen Reduced) was washed with ether to remove grease. Potassium *t*-butoxide was sublimed, block temp.  $200^{\circ}/0.02$  mm.

Chlorodiphenylphosphine (Aldrich Chemical Co. Inc.) and tetradeuterioacetic acid (Koch Light 98%) were used without purification; other reagents were purified by distillation or crystallisation.

## I PREPARATION OF ACETYLLARYLAMINES

### A o-, m- and p-t-Butylacetanilides

o-, m-, and p-t-Butylnitrobenzenes.— t-Butylbenzene (275 g., 2.05 moles) was nitrated by the method of Nelson and Brown.<sup>159</sup> Distillation of the crude product afforded a colourless liquid (16.5g.), b.p. 76-86°/23 mm., and an oil (279g.), b.p. 63-87°/0.15 mm. The latter was examined by g.l.c. (2% NPGS, 140°) and found to be a mixture of o-, m-, and p-t-butylnitrobenzenes (1.56 moles, 76%) in the approximate ratio 2:1:5. Fractional distillation through the spinning-band column yielded o-t-butylnitrobenzene, b.p. 148°/38 mm., and m-t-butylnitrobenzene, b.p. 158°/36 mm. p-t-Butylnitrobenzene, m.p. 27°, could be obtained from the residue by crystallisation from ethanol at -40°. This compound was also prepared by Dr. P.G. Hibbert.

p-t-Butylaniline.— A mixture of p-t-butylnitrobenzene (71.6 g., 0.40 mole), iron powder (89.6g.), ethanol (160g.), and water (160g.) was stirred vigorously while hydrochloric acid (sp.gr. 1.16, 9.60g.) was cautiously added. After

boiling under reflux and stirring for 14 hr., the cooled reaction mixture was made alkaline with 10% sodium hydroxide solution and filtered. The reaction flask and solid residue were washed with methanol, the washings combined with the filtrate, and much of the alcohol was removed by distillation. Water (50 ml.) and ether (150 ml.) were added to the residue, the layers separated, and the aqueous portion was extracted with ether (100 ml.). The original filtration residue was extracted with ether (100 ml.), and all the extracts were combined and dried over potassium hydroxide pellets. Evaporation of the solvent left a brown oil which was distilled from zinc dust in an atmosphere of nitrogen to yield p-t-butylaniline (55.8g., 0.375 mole, 94%), b.p. 108-10°/8 mm.

p-t-Butylacetanilide.-- Acetic anhydride (45.0g.) was gradually added to a stirred solution of p-t-butylaniline (53.4g., 0.358 mole) in acetic acid (24.0g.). The mixture was heated at 120° for 30 min. The solid which separated when the hot solution was poured into iced water (1.5 l.) was collected, washed with water, dried, and crystallised from benzene-petroleum (6:1) to give p-t-butylacetanilide (65.6g., 0.344 mole, 96%), m.p. 173-4° (lit.,<sup>153</sup> 174°).

N.m.r. (CDCl<sub>3</sub>):  $\tau$ 1.83(broad, NH), 2.55(unresolved multiplet, 4H), 7.90(Me) and 8.72(t-Bu).

The following compounds were prepared in a similar manner, but without purification of the amine:

o-t-Butylacetanilide.-- (84%), m.p. 164-5° (lit.,<sup>153</sup> 163°).

N.m.r. (CDCl<sub>3</sub>):  $\tau$  2.30-3.10 (complex, 4H), 7.86 (Me) and 8.62 (t-Bu).

m-t-Butylacetanilide.-- (92%), m.p. 101-2° (lit.,<sup>160</sup> 101.5-2.5°).

Each of the isomeric amides was shown by g.l.c. (2% NPGS, 180°) to contain less than 0.1% of any impurity.

B o- and p-t-Butyl-2,2,2-trideuterioacetanilides

Trideuterioacetyl Chloride.-- Freshly distilled phosphorus trichloride (7.56g.) was dripped into tetradeuterioacetic acid (10.0g., 0.156 mole) and the mixture was stirred at room temperature for 15 min. and then at 50° for a further 30 min. The crude acyl chloride was distilled out, treated with 2 drops of tetradeuterioacetic acid to destroy any phosphorus esters present,<sup>158</sup> and fractionally distilled to yield trideuterioacetyl chloride (7.28g., 0.089 mole, 57%), b.p. 50-52°.

o-t-Butyl-2,2,2-trideuterioacetanilide.-- Crude o-t-butyl-anilino (3.73g., 0.025 mole) was dissolved in ether (100 ml.) and triethylamine (3.40g.) added. The solution was stirred at 0° while trideuterioacetyl chloride (2.69g.) in ether (20 ml.) was added dropwise during 15 min. After stirring the mixture

for a further 2 hr. the solid material was filtered off, and dissolved in chloroform (50 ml.) and water (50 ml.). The layers were separated and the aqueous portion was extracted with chloroform (2 x 25 ml.). The organic extracts were dried over sodium sulphate, and evaporated to give a white solid which was added to that obtained by evaporation of the ethereal filtrate. Crystallisation from benzene (twice) yielded colourless needles of o-t-butyl-2,2,2-trideuterioacetanilide (4.27g., 0.022 mole, 87%), m.p. 164-5°. The n.m.r. spectrum showed no absorption at  $\tau$  7.86.

p-t-Butyl-2,2,2-trideuterioacetanilide.- This compound was prepared similarly in 90% yield, m.p. 173-4° from benzene. The n.m.r. spectrum showed no absorption at  $\tau$  7.90.

#### G 2,5-Di-t-butylacetanilide

1,4-Di-t-butyl-2-nitrobenzene.- p-Di-t-butylbenzene was nitrated as described by Legge<sup>161</sup> to yield, after crystallisation from isopropanol, 1,4-di-t-butyl-2-nitrobenzene (71%), m.p. 79-84°. A sample was recrystallised and had m.p. 84-5° (lit.,<sup>161</sup> 86-86.5°).

2,5-Di-t-butylaniline.- A mixture of the nitro compound (44.0g., 0.19 mole), iron powder (37.6g.), ethanol (38g.), and water (38g.) was stirred vigorously and hydrochloric acid (sp.gr. 1.16, 3.76g.) added. The mixture was boiled under reflux for 24 hr., made alkaline with 10% sodium hydroxide



solution, and allowed to cool to room temperature. The solid material was collected, and together with that remaining in the flask, was extracted with hot chloroform (160, 2 x 140 ml.). The filtered extracts were concentrated to a yellow residue which crystallised from ethanol to give pale yellow 2,5-di-*t*-butylaniline (32.4g., 0.16 mole, 85%), m.p. 103-4° (lit.,<sup>162</sup> 103-4°).

2,5-Di-*t*-butylacetanilide.— 2,5-Di-*t*-butylaniline (14.3g., 0.070 mole) and acetic anhydride (9.70g.) were heated on a steam-bath for 8 min. Water (80 ml.) was added, the mixture shaken vigorously, and the precipitate collected, washed with water, and crystallised from isopropanol to give 2,5-di-*t*-butylacetanilide (15.9g., 0.064 mole, 91%), m.p. 158-9° (lit.,<sup>161</sup> 155.6-156.4°). (Found: C, 77.3; H, 10.05. Calc. for C<sub>16</sub>H<sub>25</sub>NO: C, 77.7; H, 10.2%). Examination by g.l.c. (10% SIL, 198°) revealed no impurities.

D 1,4-Diacetamido-2,5-di-*t*-butylbenzene

1,4-Di-*t*-butyl-2,5-dinitrobenzene.— This compound was prepared by nitration of *p*-di-*t*-butylbenzene, using the method of Carpenter and Easter,<sup>163</sup> who incorrectly<sup>164</sup> assigned the structure 2,5-di-*t*-butyl-1,3-dinitrobenzene to their product. The crude reaction product was examined by g.l.c. and found to contain five components, A-E (retention time in min. and approximate weight % given), of which B and C were incompletely resolved: A(2.25, 3%), B(7.15, 54-64%), C(7.70, 10-20%),

D(12.1, 5%) and E(13.85, 18%). Three crystallisations from ethanol afforded 1,4-di-*t*-butyl-2,5-dinitrobenzene (B, 25%), m.p. 194-5°. (Found: C, 60.0; H, 7.1. Calc. for  $C_{14}H_{20}N_2O_4$ : C, 60.0; H, 7.2%).

N.m.r. ( $CDCl_3$ ):  $\tau$  2.48(s, 2H) and 8.58(s, 18H, *t*-Bu).

The material isolated by Carpenter and Easter had m.p. 193-3.5°.

2,5-Di-*t*-butyl-*p*-phenylenediamine.— A mixture of 1,4-di-*t*-butyl-2,5-dinitrobenzene (24.8g., 0.089 mole), iron powder (36.8g.), hydrochloric acid (sp.gr. 1.16, 3.68g.), ethanol (69g.), and water (73g.) was stirred vigorously and boiled under reflux for 42 hr. Application of the work-up procedure described for the preparation of 2,5-di-*t*-butylaniline yielded 2,5-di-*t*-butyl-*p*-phenylenediamine (18.8g., 0.085 mole, 97%), m.p. 171-3°. A sample crystallised from ethanol had m.p. 171-2°.

N.m.r. ( $CCl_4$ ):  $\tau$  3.39(s, 2H), 6.59(s, 4H,  $NH_2$ ) and 8.61 (s, 18H, *t*-Bu).

Legge<sup>161</sup> has reported m.p. 171-2° for 2,5-di-*t*-butyl-*m*-phenylenediamine.

1,4-Diacetamido-2,5-di-*t*-butylbenzene.— Acetic anhydride (79g.) was added in portions to the diamine (20.3g., 0.092 mole) and the suspension was heated on a steam-bath for 8 min. Water (300 ml.) was added, the mixture shaken vigorously, and the resulting white solid was collected. This material,



which was only slightly soluble in common solvents, was boiled with acetic acid (800 ml.) for 1 hr., and the undissolved solid collected on a filter, washed with methanol, and sublimed at  $260-90^{\circ}$  (block temp.)/0.01 mm. to yield colourless 1,4-diacetamido-2,5-di-*t*-butylbenzene (22.0g., 0.072 mole, 78%), m.p.  $392-4^{\circ}$ . (Found: C, 70.6; H, 9.45; N, 9.2. Calc. for  $C_{18}H_{28}N_2O_2$ : C, 71.0; H, 9.3; N, 9.2%). N.m.r. (2% w/v in hexadeuteriodimethylsulphoxide):  $\tau$  8.74 (*t*-Bu). Legge<sup>161</sup> has reported m.p.  $368-70^{\circ}$  for 1,3-diacetamido-2,5-di-*t*-butylbenzene.

E 1,3-Diacetamido-2,5-di-*t*-butylbenzene

Attempted Isolation of 2,5-Di-*t*-butyl-1,3-dinitrobenzene.-

The crystallisation mother liquors from several preparations of 1,4-di-*t*-butyl-2,5-dinitrobenzene (employing a total of ca. 340g. *p*-di-*t*-butylbenzene) were evaporated, and portions of the residue fractionally crystallised from ethanol, isopropanol, acetic acid, and combinations of petroleum, benzene, carbon tetrachloride and nitromethane. In all cases, later crops of crystals appeared homogeneous and melted over a narrow range, but were seen by g.l.c. (2% NPGS,  $176^{\circ}$  and 10% PEGA,  $200^{\circ}$ ) to contain at least 20% 1,4-di-*t*-butyl-2,5-dinitrobenzene. A total of 26.8g. of the isomeric mixture, m.p.  $139-40^{\circ}$ , was obtained.

N.m.r. ( $CDCl_3$ ):  $\tau$  2.50(s, 2H) and 8.53, 8.59 and 8.62 (total 18H, *t*-Bu).

The last three absorptions had integrals in the ratio 1:0.8:1. Bell and Buck<sup>164</sup> have reported m.p. 141° for 2,5-di-*t*-butyl-1,3-dinitrobenzene.

1,3-Diacetamido-2,5-di-*t*-butylbenzene.— The mixture of dinitro compounds (10.6g.) was reduced in a similar manner to 1,4-di-*t*-butyl-2,5-dinitrobenzene, giving a brown oily solid which was stirred with acetic acid (6.2g.) and acetic anhydride (8.3g.) at 110° for 1 hr. A brown tar separated when the mixture was poured into iced water (400 ml.). The aqueous portion was decanted and the tar boiled with ethanol (15 ml.). Water (3 ml.) was added and the resulting brown powder was collected and boiled with ethanol (50 ml.). The hot suspension was freed from insoluble material, and the filtrate set aside at -10° to yield colourless needles of 1,3-diacetamido-2,5-di-*t*-butylbenzene (0.92g.), m.p. 321°. (Found: C, 70.5; H, 9.3.  $C_{18}H_{28}N_2O_2$  requires C, 71.0; H, 9.3%).

N.m.r. (10% w/v in hexadeuteriodimethylsulphoxide):  $\tau$  3.09(s, 2H), 6.63(s, 2H, NH), 8.02(s, 6H, Me), 8.63(9H, *t*-Bu) and 8.79(9H, *t*-Bu).

No absorption was detected at 8.74.

F 4-Acetoxy-2,5-di-*t*-butylacetanilide.

2,5-Di-*t*-butyl-4-nitrosophenol.<sup>165</sup>— A solution of 2,5-di-*t*-butyl-*p*-benzoquinone (66.0g., 0.30 mole) and hydroxylamine hydrochloride (31.3g.) in ethanol (850 ml.)

was boiled under reflux in an atmosphere of nitrogen for 30 hr. The cooled reaction mixture was filtered, the filtrate added to 0.5N - sodium hydroxide solution (900 ml.) and the resulting brown solid collected. Acidification of the filtrate produced no additional solid. Three crystallisations from mixtures of benzene, ethanol and cyclohexane yielded yellow 2,5-di-*t*-butyl-4-nitrosophenol (29.6g., 0.13 mole, 42%), m.p.  $209-10^{\circ}$  (lit., <sup>165</sup>  $209^{\circ}$ ).

4-Amino-2,5-di-*t*-butylphenol. - Reduction of the nitrosophenol as described for the reduction of 2,5-di-*t*-butylnitrobenzene gave crude 4-amino-2,5-di-*t*-butylphenol (100%). A sample crystallised from methanol had m.p.  $208-9^{\circ}$ .

N.m.r. (acetone):  $\tau$  2.75(broad, OH), 3.31(s, 1H), 3.40(s, 1H) and 6.25(broad, NH<sub>2</sub>)

(8% w/v in CDCl<sub>3</sub>):  $\tau$  8.62(18H, *t*-Bu).

4-Acetoxy-2,5-di-*t*-butylacetanilide. - The aminophenol (12.2g., 0.055 mole) was stirred with acetic anhydride (48g.), and pyridine (8.70g.) added in portions. The resulting solid mass was heated at  $100^{\circ}$  and acetic acid (20 ml.) added to give a clear solution which was heated for a further 45 mins. and then poured into iced water (1.6 l.). The precipitated material was crystallised from acetic acid to give colourless 4-acetoxy-2,5-di-*t*-butylacetanilide (14.2g., 0.047 mole, 85%), m.p.  $236-7^{\circ}$ . (Found: C, 70.8; H, 8.9; N, 4.4.

$C_{18}H_{27}NO_3$  requires C, 70.8; H, 8.9; N, 4.6%.

N.m.r. ( $CDCl_3$ ):  $\tau$  2.54(s, 1H), 3.05(s, 1H), 7.69(Me), 7.84(Me)  
8.64(t-Bu) and 8.68(t-Bu).

I.r. (Nujol): 3270(N-H); 1765 and 1660  $cm^{-1}$  (C=O).

G o-Acetamidophenyldiphenylphosphine Oxide

Ethyl Diphenylphosphonite.-- This substance was prepared in 91% yield by the method of Rabinowitz and Pellon<sup>166</sup> and had b.p. 104-6°/0.35 mm.

Diphenyl(o-nitrophenyl)phosphine Oxide.<sup>167</sup> - A solution of o-dinitrobenzene (34.3g., 0.20 mole) in dimethylformamide (120 ml.) was stirred at 0° in an atmosphere of nitrogen. Ethyl diphenylphosphonite (73.9g.) dissolved in dimethylformamide (60 ml.) was added dropwise during 2 hr. Stirring was continued for a further 1 hr., yielding pale brown crystals of diphenyl(o-nitrophenyl)phosphine oxide (40.0g., 0.12 mole, 60%), m.p. 227-8° (lit.,<sup>167</sup> 225°).

o-Aminophenyldiphenylphosphine Oxide.<sup>167</sup> - The nitro compound (24.0g., 0.074 mole), iron powder (14.5g.), hydrochloric acid (sp.gr. 1.16, 1.6g.), ethanol (290 ml.) and water (290 ml.) were stirred efficiently at the reflux temperature for 24 hr. The hot mixture was made alkaline with 10% sodium hydroxide solution and filtered through 'Hyflo-Supercel'. The filtrate, when cold, deposited a pink solid which was crystallised from ethanol-water-acetone

(2:2:1) to yield colourless o-aminophenyldiphenylphosphine oxide (16.0g., 0.047 mole, 64%), m.p.  $163-4^{\circ}$  (lit.,<sup>167</sup>  $163-4^{\circ}$ ).

o-Acetamidophenyldiphenylphosphine Oxide.~ The amine (8.21g., 0.028 mole) was acetylated in the same manner as p-*t*-butylaniline to yield, after repeated crystallisation from light petroleum (b.p.  $60-80^{\circ}$ ) - benzene (1:1), very pale pink needles, m.p.  $128-30^{\circ}$ . The n.m.r. spectrum contained a strong absorption at  $\tau$  2.65(benzene) which had disappeared after the crystals had been heated at  $70^{\circ}/0.04$  mm. There remained amorphous o-acetamidophenyldiphenylphosphine oxide (7.21g., 0.022 mole, 77%), m.p.  $129-30^{\circ}$ . (Found: C, 71.5; H, 5.5; N, 4.3.  $C_{20}H_{18}NO_2P$  requires C, 71.6; H, 5.4; N, 4.2%). N.m.r. ( $CDCl_3$ ):  $\tau$  -1.07(broad, NH), 1.25-3.15(complex, 14H) and 7.90(Me).

I.r. (Nujol): 1700 (C=O) and  $1310\text{ cm.}^{-1}$  (P=O).

#### H Diethyl o-Acetamidophenylphosphonate

Diethyl o-Nitrophenylphosphonate.<sup>167</sup>~ A mixture of o-dinitrobenzene (67.2g., 0.40 mole), triethyl phosphite (133g.), and acetonitrile (500 ml.) was boiled under reflux in an atmosphere of dry nitrogen for 11 hr. Volatile material was removed by distillation under reduced pressure and the residue fractionally distilled to yield diethyl o-nitrophenylphosphonate (68.5g., 0.265 mole, 66%), b.p.  $138-9^{\circ}/0.15$  mm., which solidified on standing. Crystallisation

from ether-petroleum (1:1) gave stout, pale yellow needles (62.3g.), m.p.  $53-4^{\circ}$  (lit.,<sup>167</sup>  $56^{\circ}$ ).

N.m.r. spectrum: see Appendix.

Diethyl o-Aminophenylphosphonate.<sup>168</sup> - The nitro compound (60.9g., 0.235 mole), acetic acid (32 ml.) and water (370 ml.) were mixed and efficiently stirred, without heating, while iron powder (145g.) was cautiously added in small portions. The mixture was heated at  $60-70^{\circ}$  for 30 min. and at  $80^{\circ}$  for 45 min., vigorous stirring being maintained throughout. When cool, the mixture was filtered through 'Hyflo-Supercel', the residue washed with water, and the combined filtrate and washings neutralised ( $\text{KHCO}_3$ ) and extracted with chloroform (800, 2 x 400 ml.). The filter cake was extracted ( $\text{CHCl}_3$ ) and the combined extracts were concentrated to 500 ml. and dried over magnesium sulphate. The remaining solvent was removed and the residue distilled in an atmosphere of nitrogen to yield diethyl o-aminophenylphosphonate (51.0g., 0.223 mole, 95%), b.p.  $103-8^{\circ}/0.02$  mm. A portion of the product, crystallised from ether at  $-40^{\circ}$ , had m.p.  $32-3^{\circ}$  (lit.,<sup>168</sup>  $28-9^{\circ}$ ).

N.m.r. spectrum: see Appendix.

Diethyl o-Acetamidophenylphosphonate. - Acetylation of the amino (41.2g., 0.180 mole) by the method described for the preparation of p-t-butylacetanilide gave, after



crystallisation from ether at  $-30^{\circ}$ , colourless diethyl  
o-acetamidophenylphosphonate (41.5g., 0.154 mole, 86%),  
 m.p.  $37-9^{\circ}$  (lit.,<sup>168</sup>  $33-6^{\circ}$ ).

N.m.r. spectrum: see Appendix.

I.r. (melt): 3260 (and small bands, N-H), 1700 (C=O) and  
 $1300\text{ cm.}^{-1}$  (P=O).

No impurities were detected by g.l.c. examination (3% CAR,  $173^{\circ}$ ).

#### I Other Acetylarylamines

The following compounds were prepared from commercially  
 available amines by the method of acetylation described for  
 the preparation of p-*t*-butylacetanilide:

o-chloroacetanilide (65% yield), m.p.  $87-8^{\circ}$  (lit.,<sup>169</sup>  $87^{\circ}$ ),

m-chloroacetanilide (88% yield), m.p.  $71-2^{\circ}$  (lit.,<sup>169</sup>  $72-3^{\circ}$ ),

o-trifluoromethylacetanilide (81% yield), m.p.  $93-4^{\circ}$  (lit.,<sup>170</sup>  $94^{\circ}$ ).

Acetylation of p-acetamidophenol by the procedure employed  
 for the preparation of 4-acetoxy-2,5-di-*t*-butylacetanilide  
 yielded p-acetoxyacetanilide (84%), m.p.  $152-3^{\circ}$  (lit.,<sup>171</sup>  $152^{\circ}$ ).

Attempts to convert o-trifluoromethylacetanilide into  
o-trichloromethylacetanilide by the reaction with acetyl chloride  
 and aluminium trichloride<sup>172,173</sup> gave N-acetylanthranilic acid  
 as the only isolable product.

Acetanilide, m.p.  $114-5^{\circ}$ , and p-chloroacetanilide,  
 m.p.  $178-9^{\circ}$ , were purified by crystallisation.

## II PREPARATION OF PHENOLS AND ARYL ACETATES

### A 2,5-Di-t-butylphenol

2,5-Di-t-butylaniline was diazotised by the method of Carpenter et. al.<sup>162</sup> The diazonium salt decomposed to yield, after steam-distillation and crystallisation from ethanol, 2,5-di-t-butylphenol (42%), m.p. 117-9° (lit.,<sup>162</sup> 118-9°). The i.r. spectrum contained a weak band at 3380 cm.<sup>-1</sup> indicating the presence of unreacted amine. A portion of the impure phenol was dissolved in ether, and hydrogen chloride passed through the solution for 1 hr. A small amount of solid material was filtered off and the filtrate evaporated to yield, from light-petroleum (b.p. 60-80°), colourless needles of 2,5-di-t-butylphenol, m.p. 121-2°.

I.r. (Nujol): 3510 cm.<sup>-1</sup> (O-H). No band at 3380 cm.<sup>-1</sup>

### B 2,5-Di-t-butylphenyl Acetate

2,5-Di-t-butylphenol (1.00g., 0.0048 mole) was dissolved with warming in acetic anhydride (1.50g.), sulphuric acid (sp.gr. 1.84, 1 drop) added, and the solution heated on a steam-bath for 10 min. The precipitate which formed when the mixture was poured onto crushed ice (5g.) was collected, washed with water, dried, and crystallised from light-petroleum (b.p. 60-80°) at -40° to yield colourless needles of 2,5-di-t-butylphenyl acetate (0.28g., 0.0012 mole, 25%), m.p. 52-3°. (Found: C, 77.6; H, 9.4. C<sub>16</sub>H<sub>24</sub>O<sub>2</sub> requires C, 77.4; H, 9.7%).



N.m.r. ( $\text{CCl}_4$ ):  $\tau$  2.71(d,  $\text{H}_3$ ), 2.92(dd,  $\text{H}_4$ ), 3.06(dd,  $\text{H}_6$ ),  
 7.75(Me) and 8.67 (unresolved d, 18H,  
 t-Bu).  $J_{3-4}$  8.4,  $J_{4-6}$  1.8, and  $J_{3-6}$  ca.  
 0.0 c./sec.

I.r. (Nujol): 1760  $\text{cm}^{-1}$

C 2,5-Di-t-butylhydroquinone Diacetate

2,5-Di-t-butylhydroquinone was prepared from hydroquinone and t-butanol following the procedure of Oesper et. al.,<sup>174</sup> and acetylated<sup>175</sup> without purification to yield, after crystallisation from benzene, 2,5-di-t-butylhydroquinone diacetate (33%), m.p. 175-6° (lit.,<sup>175</sup> 173-4°).

N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  2.98(s, 2H), 7.67(s, 6H, Me) and 8.66(s, 18H, t-Bu).

I.r. (Nujol): 1760  $\text{cm}^{-1}$  (C=O).

D Diphenyl(o-hydroxyphenyl)phosphine Oxide

o-Aminophenyldiphenylphosphine oxide (0.78g., 0.0025 mole) was dissolved in warm 20% hydrochloric acid (1.2 ml.) and the stirred solution cooled to 0°. Sodium nitrite (0.19g.) in water (0.6 ml.) was added dropwise, when a yellow solid was deposited. Water (12 ml.) was added and the suspension was warmed at 50° for 10 min. The solid material was filtered off and crystallised from ethanol and from nitromethane to yield diphenyl(o-hydroxyphenyl)phosphine oxide (0.23g., 0.0008 mole, 32%), m.p. 227-9°.

### E o-Acetoxyphenyldiphenylphosphine Oxide

A mixture of diphenyl(o-hydroxyphenyl)phosphine oxide (0.22g., 0.75 mmole), acetic anhydride (0.5 ml.) and sulphuric acid (sp.gr. 1.84, 1 drop) was heated on a steam-bath for 20 min. The solution was poured onto crushed ice (20g.) to give a white solid which, crystallised from light-petroleum (b.p. 60-80°)-benzene (1:1), afforded pale yellow needles of o-acetoxyphenyldiphenylphosphine oxide (0.18g., 0.54 mmole, 72%), m.p. 155-6°. (Found: C, 71.8; H, 5.2.  $C_{20}H_{17}O_3P$  requires C, 71.4; H, 5.1%).

N.m.r. ( $CDCl_3$ ):  $\tau$  1.99 - 2.93 (complex) and 8.27 (Me).

I.r. (Nujol): 1765 (C=O) and 1200  $cm^{-1}$  (P=O).

### F Diethyl o-Hydroxyphenylphosphonate

A solution of diethyl o-aminophenylphosphonate (3.44g., 0.015 mole) in 8% hydrochloric acid (18 ml.) was stirred at -5° while freshly distilled ethyl nitrite (1.50g.) was run in during 2 min. Stirring was continued, at 0°, for a further 20 min. The solution was poured, with stirring, into water (100 ml.) at 65°, and the mixture maintained at that temperature for 15 min. After cooling in ice, the mixture was extracted with benzene (4 x 14 ml.) and the combined extracts were washed with 10% sodium hydrogen carbonate solution, dried over sodium sulphate, and concentrated to a yellow oil (3.14g.). Distillation afforded diethyl o-hydroxyphenylphosphonate

(2.92g., 0.013 mole, 85%), b.p.  $74-6^{\circ}/0.02$  mm., which solidified on standing. Colourless crystals, m.p.  $40-41^{\circ}$ , were formed from petroleum containing a little ether at  $-20^{\circ}$ . (Found: C, 52.4; H, 6.8.  $C_{10}H_{15}PO_4$  requires C, 52.2; H, 6.6%).

N.m.r. spectrum: see Appendix.

I.r. (melt): 3140-2600 (several bands), 1610, 1600 and 1580 (O-H) and  $1200\text{ cm.}^{-1}$  (P=O).

G Diethyl o-Acetoxyphenylphosphonate

The phenol (1.15g., 0.0050 mole) was acetylated as described for diphenyl(o-hydroxyphenyl)phosphine oxide. The crude product was extracted with ether (25, 2 x 15 ml.) and the combined extracts were washed with 5% sodium hydroxide solution and water, and dried over magnesium sulphate. Distillation yielded colourless diethyl o-acetoxyphenylphosphonate (0.70g., 0.0026 mole, 52%), b.p.  $83-5^{\circ}/0.02$  mm. (Found: C, 52.6; H, 6.6.  $C_{12}H_{17}PO_5$  requires C, 52.9; H, 6.3%).

N.m.r. spectrum: see Appendix.

I.r. (liquid): 1770 (C=O) and  $1250\text{ cm.}^{-1}$  (P=O).

H Diethyl m-Hydroxyphenylphosphonate

A stirred solution of m-iodophenol (6.26g., 0.031 mole) in triethyl phosphite (100 ml.) was irradiated with u.v. light for 44 hr. at  $10^{\circ}$  in an atmosphere of dry nitrogen. Volatile material was removed by evaporation under reduced pressure, and then by vacuum-distillation, bath temp. to  $120^{\circ}/0.03$  mm. The

residue, dissolved in ether (25 ml.) was extracted with 10% sodium carbonate solution (3 x 20 ml.) and the extracts were acidified with hydrochloric acid (sp. gr. 1.16) when an oil separated. Extraction with ether (40, 3 x 20 ml.) afforded a colourless solution which was dried over sodium sulphate and evaporated to yield viscous diethyl m-hydroxyphenylphosphonate (1.81g., 0.008 mole, 26%), b.p. 185-95° (block temp.)/0.02 mm.

(Found: C, 52.0; H, 6.9.  $C_{10}H_{15}PO_4$  requires C, 52.2; H, 6.6%).

N.m.r. spectrum: see Appendix.

I.r. (liquid): 3170-2590 (several bands), 1600, 1580 (O-H) and 1220  $cm.^{-1}$  (P=O).

#### I Diethyl m-Acetoxyphenylphosphonate

Diethyl m-hydroxyphenylphosphonate (1.12g., 0.0049 mole) was acetylated by the method described for the preparation of diethyl o-acetoxyphenylphosphonate, but with a reaction time of 1 hr., to yield m-acetoxyphenylphosphonate (0.94g., 0.0034 mole, 70%), b.p. 130-40° (block temp.)/0.02 mm. (Found: C, 52.7; H, 6.6.  $C_{12}H_{17}PO_5$  requires C, 52.9; H, 6.3%).

N.m.r. spectrum: see Appendix.

I.r. (liquid): 1770 (C=O) and 1255  $cm.^{-1}$  (P=O)

#### J Other Aryl Acetates

Acetylation of hydroquinone following the procedure of Olcott<sup>176</sup> yielded hydroquinone diacetate (11%), m.p. 121-2° (lit.,<sup>176</sup> 123-4°); and hydroquinone monoacetate (3%), m.p. 58-9° (lit.,<sup>176</sup> 62-3°).

m-Chlorophenol was acetylated by Chattaway's method<sup>177</sup> to give m-chlorophenyl acetate (78%), b.p. 81-2°/2.2 mm. I.r. 1775 cm.<sup>-1</sup> (C=O).

o-*t*-Butylphenyl acetate, b.p. 116°/12 mm., was prepared from the phenol in a manner similar to that of the preparation of 2,5-di-*t*-butylphenyl acetate. I.r. 1770 cm.<sup>-1</sup> (C=O).

Phenyl acetate, b.p. 195°, p-*t*-butylphenyl acetate, b.p. 130°/16 mm., and m-*t*-butylphenyl acetate, m.p. 42-3° (lit.,<sup>178</sup> 42-3°) were purified by distillation or recrystallisation.

1,3-Diacetamido-2,5-di-*t*-butylbenzene was hydrolysed and the diamine tetrazotised. When the clear solution of tetrazonium salt was dripped into a large volume of 5% sulphuric acid at 100°, polymeric material resulted. No 2,5-di-*t*-butylresorcinol was obtained when this brown powder was heated in a sublimation tube at 170°/0.03 mm.

### III PREPARATION OF BIARYLS

#### A 2-*t*-Butylbiphenyl

A solution of dry dibenzoyl peroxide (14.5g., 0.060 mole) in *t*-butylbenzene (107g.) was heated at 80° for 3 days in an atmosphere of dry nitrogen. The excess of *t*-butylbenzene was evaporated under reduced pressure, and the residue distilled to

give a colourless liquid (4.44g.), b.p.  $40-92^{\circ}/0.05$  mm. This was found by g.l.c. examination (20% APL,  $233^{\circ}$ ) to consist of three components, A (retention time 18.1 min.), B (27.0 min.) and C (33.7 min.), in the approximate ratio 1:3:2. The retention times of B and C were identical to those of authentic specimens of 3- and 4-t-butylbiphenyl. Preparative g.l.c. (Aerograph A.700, 8 ft. x 0.375 in. i.d. aluminium column containing 20% APL on celite at  $233^{\circ}$ ) allowed isolation of a sample of component A, which was crystallised from ethanol at  $-40^{\circ}$  to yield 2-t-butylbiphenyl, m.p.  $36-7^{\circ}$  (lit.,<sup>153</sup>  $31-4^{\circ}$ ).

N.m.r. ( $\text{CCl}_4$ ):  $\tau$  2.40-3.25 (complex, 9H) and 8.82 (t-Bu).

B Diethyl 2-Biphenylphosphonate

2-Iodobiphenyl.— 2-Aminobiphenyl was diazotised and the diazonium chloride allowed to react with potassium iodide, following the procedure of Gilman et. al.,<sup>179</sup> to give 2-iodobiphenyl (88%), b.p.  $83-6^{\circ}/0.04$  mm.

Diethyl 2-Biphenylphosphonate.— A stirred solution of 2-iodobiphenyl (8.40g., 0.030 mole) in triethyl phosphite (100 ml.) was irradiated with u.v. light for 3 hr. at  $0^{\circ}$  in an atmosphere of dry nitrogen. Volatile material was removed under reduced pressure and the residue fractionally distilled to yield a colourless liquid (6.98g.), b.p.  $112-18^{\circ}/0.02$  mm. Crystallisation from ether-petroleum (1:1) afforded diethyl

2-biphenylphosphonate (5.09g., 0.018 mole, 59%), m.p.

34-7°. (Found: C, 66.0; H, 6.7.  $C_{16}H_{19}O_3P$  requires C, 66.2; H, 6.6%).

N.m.r. spectrum: see Appendix.

I.r. (melt): 1240  $cm^{-1}$  (P=O).

#### C Other Biaryls

3-Chlorobiphenyl was given by Professor D.H. Hey, F.R.S.

2,5-Di-*t*-butylbiphenyl was that prepared by Cadogan, Hey and Williams.<sup>153</sup> 2-Phenylfuran was prepared by Dr. D.L. Brydon.

3-Acetoxybiphenyl, m.p. 33-4° (lit.,<sup>180</sup> 34-34.2°); 4-Acetoxybiphenyl, m.p. 85-6° (lit.,<sup>169</sup> 88-9°); biphenyl, m.p. 68-9° (lit.,<sup>169</sup> 71°); 2-chlorobiphenyl, m.p. 31° (lit.,<sup>169</sup> 32°); 4-chlorobiphenyl, m.p. 75-6° (lit.,<sup>169</sup> 77°); and 4-hydroxybiphenyl, m.p. 167-8° (lit.,<sup>169</sup> 164-5°) were purified by recrystallisation.

### IV PREPARATION OF ARYNOPHILES

#### A 2,5-Dimethylfuran

The dehydration of acetonylacetone with freshly distilled acetic anhydride and anhydrous zinc chloride, following the procedure of Gaertner and Tonkyn,<sup>184</sup> gave 2,5-dimethylfuran (63%), b.p. 93-5°, which was further purified by fractional distillation from sodium wire in an atmosphere of dry nitrogen,



b.p.  $93.5^{\circ}$  (lit.,<sup>184</sup>  $92.5-94^{\circ}$ ), immediately before use.

B 2-(p-t-Butylphenyl)-3,4,5-triphenylcyclopentadienone

p-t-Butylphenylacetonitrile.— Potassium cyanide (16.3g.) and water (12 ml.) were stirred on a steam-bath until most of the solid had dissolved. A solution of p-t-butylbenzyl chloride (36.5g., 0.20 mole) in ethanol (34 ml.) was dripped in during 30 min., and heating with stirring continued for a further 6 hr., when g.l.c. examination (2% NPGS,  $150^{\circ}$ ) revealed that the reaction was complete. The precipitated potassium chloride was filtered off from the cold reaction mixture, washed with ethanol (30 ml.), and the filtrate and washings were combined. Fractional distillation through a vacuum-jacketed Vigreux column yielded p-t-butylphenylacetonitrile (29.6g., 0.17 mole, 85%). b.p.  $121-8^{\circ}/0.4$  mm. (lit.,<sup>181</sup>  $149-53^{\circ}/16$  mm.).

I.r. (liquid):  $2240(\text{C}\equiv\text{N})$ ;  $1390$  and  $1360$   $\text{cm}^{-1}$  (t-Bu).

p-t-Butylphenylacetic Acid.— The nitrile (28.9g., 0.165 mole), sulphuric acid (sp.gr. 1.84, 42g.) and water (32g.) were stirred vigorously and boiled under reflux for 12 hr. A white solid was precipitated when the mixture was poured, with agitation, into iced water (200 ml.). The aqueous phase was decanted from the solid, which was washed with water and dissolved in ether (150 ml.). This solution was washed with water, dried over magnesium sulphate, and



evaporated to a colourless oil (35.4g.). Crystallisation from petroleum yielded p-t-butylphenylacetic acid (20.2g., 0.105 mole, 64%), m.p. 79-80° (lit.,<sup>181</sup> 78-9°).

p-t-Butylphenylacetyl Chloride.-- p-t-Butylphenylacetic acid (32.6g., 0.17 mole) was stirred with pure thionyl chloride (43g.) at 50° for 1 hr. and at the reflux temperature for 1 hr. The excess of thionyl chloride was distilled out, and portions of dry benzene (3 x 30 ml.) were distilled from the residue, which was then itself distilled in an atmosphere of nitrogen to yield violet p-t-butylphenylacetyl chloride (31.4g., 0.15 mole, 88%), b.p. 96-9°/1.3mm.

I.r. (liquid): 1800 (C=O); 1395 and 1365 cm.<sup>-1</sup> (t-Bu).

1-(p-t-Butylphenyl)-3-phenylpropan-2-one.-- This compound was prepared by a method based on the experiments of Elderfield and Burgess.<sup>182</sup>

Magnesium (9.24g.) and ether (40 ml.) were stirred under dry nitrogen, a crystal of iodine was added, and a portion (10 ml.) of a solution of benzyl chloride (48.1g., 0.38 mole) in ether (185 ml.) was run in. When the reaction commenced, the remainder of the solution was dripped in during 30 min., and stirring continued for a further 15 mins. After boiling under reflux for 15 min., the mixture was cooled in an ice-bath, and insoluble matter removed by filtration, in a stream of dry nitrogen, through a glass-wool plug. The filtrate was

diluted with ether (600 ml.) and stirred very efficiently at 0° in an atmosphere of nitrogen while cadmium chloride (55.8g.) was added in ten portions at 1 min. intervals. Stirring was continued at 0° for a further 2 hr., and then a solution of p-t-butylphenylacetyl chloride (31.4g., 0.149 mole) in ether (120 ml.) was added during 10 min. The mixture was stirred at 0° for 8 hr., and was then poured into an agitated mixture of 20% sulphuric acid (120 ml.) and crushed ice (300g.). The layers were separated, the aqueous layer was extracted with ether (2 x 100 ml.), and the combined ether extracts were washed with water (200 ml.) and 10% sodium hydrogen carbonate solution (200 ml.) and left to stand overnight. The solution was then washed with more bicarbonate solution (4 x 50 ml.), the washings were extracted with ether (2 x 50 ml.), and all the ether extracts were combined, washed with water (200 ml.), and dried over sodium sulphate. Evaporation of the solvent left a yellow oil (50.5g.) which gave, by fractional distillation in an atmosphere of nitrogen, a colourless liquid (36.8g.), b.p. 141-3°/0.18 mm. Crystallisation from petroleum at -40° afforded 1-(p-t-butylphenyl)-3-phenylpropan-2-one (32.6g., 0.123 mole, 82%), m.p. 32-3°. (Found: C, 85.8; H, 8.2.  $C_{19}H_{22}O$  requires C, 85.7; H, 8.3%).

N.m.r. ( $CCl_4$ ):  $\tau$  2.51-3.05 (complex, 9H), 6.42(-CH<sub>2</sub>-), 6.47(-CH<sub>2</sub>-) and 8.69(t-Bu).

I.r. (melt): 1710 ( $\text{C}=\text{O}$ ); 1395 and 1365  $\text{cm}^{-1}$  (t-Bu).

2-(p-t-Butylphenyl)-3,4,5-triphenylcyclopentadienone.-

The ketone (15.96g., 0.060 mole) and benzil (12.60g., 0.060 mole) were dissolved, with warming in ethanol (125 ml.). The solution was heated under reflux to a temperature slightly below the b.p., and swirled while potassium hydroxide (1.25g.) in ethanol (12.5 ml.) was cautiously added during 10 min. After boiling for 20 min. the purple mixture was allowed to cool, and the solid material filtered off and washed with ethanol. Crystallisation from benzene-ethanol (1:1) yielded dark indigo 2-(p-t-butylphenyl)-3,4,5-triphenylcyclopentadienone (22.8g., 0.052 mole, 86%). A sample gave fine needles, m.p. 225-7°, from acetone. (Found: C, 89.7; H, 6.7.  $\text{C}_{33}\text{H}_{28}\text{O}$  requires C, 90.0; H, 6.4%).

N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  2.55-3.20 (complex, 19H) and 8.73 (t-Bu).

I.r. (Nujol): 1705  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).

C 2,3,4,5-Tetraphenylcyclopentadienone

The condensation of equimolar amounts of benzil and dibenzyl ketone under conditions similar to those that were employed in the previous synthesis yielded, after crystallisation from benzene-ethanol (1:1), purple 2,3,4,5-tetraphenylcyclopentadienone (83%), m.p. 217-8° (lit.,<sup>183</sup> 218°).

D Other Arynophiles

Phenyl azide was prepared from phenyl hydrazine by the

method of Lindsay and Allen.<sup>185</sup> The crude product was distilled from a warm water-bath, in an apparatus surrounded by wire gauze, to give the pure azide (74%), b.p. 27-9°/1.0 mm., which was dried over molecular sieve.

Anthracene (B.D.H. 'blue fluorescence') was dried over phosphorus pentoxide in a vacuum-desiccator.

Furan was distilled, dried over molecular sieve, and redistilled from sodium wire, b.p. 31°, immediately before use.

## V PREPARATION OF ARYNE SOURCES

### A p-Bromo-t-butylbenzene

t-Butylbenzene was brominated by the method of Marvel et. al.<sup>188</sup> Fractional distillation of the crude reaction product through a Vigreux column gave p-bromo-t-butylbenzene (66%), b.p. 106-10°/20 mm.

N.m.r. ( $\text{CCl}_4$ ):  $\tau$  2.72 (centre of AA'BB', 4H) and 8.70 (t-Bu).

### B o-Bromo-t-butylbenzene

2-Bromo-1-t-butyl-4-nitrobenzene.— p-t-Butylnitrobenzene was brominated in sulphuric acid containing silver sulphate as described by Crawford and Stewart<sup>186</sup> to yield 2-bromo-1-t-butyl-4-nitrobenzene (82%), m.p. 92-4° (lit.,<sup>186</sup> 94°).

3-Bromo-4-t-butylaniline.— A mixture of the nitro compound (80.0g., 0.31 mole), iron powder (65g.), ethanol

(275 ml.) and hydrochloric acid (sp.gr. 1.16, 11.3g.) was stirred and boiled under reflux for 4 hr. The mixture was allowed to cool and an ethanolic solution of potassium hydroxide (6.6g.) added. Solid material was filtered off and washed with ethanol, and the combined filtrate and washings evaporated to give, as a brown oil, 3-bromo-4-*t*-butylaniline (59.1g., 0.26 mole, 84%), which was not purified.

*o*-Bromo-*t*-butylbenzene.— The amine was deaminated by treatment of the diazonium salt with hypophosphorous acid (500 ml.) as described by Crawford and Stewart.<sup>186</sup> The crude product was fractionally distilled through the spinning-band column to yield *o*-bromo-*t*-butylbenzene (25.1g., 0.12 mole, 46%), b.p. 130–32°/40–41 mm. (lit.,<sup>186</sup> 96–8°/12 mm.). N.m.r. (CCl<sub>4</sub>):  $\tau$  2.38–3.26 (complex, 4H) and 8.50 (*t*-Bu). I.r. (0.1 mm. film): 1955, 1920, 1890, 1835, 1800, 1700, and 1670cm.<sup>-1</sup>

the position and relative intensities  
being as expected for an *o*-disubstituted  
benzene.<sup>187</sup>

C 1,4-Dibromo-2,5-di-*t*-butylbenzene

Bromination of *p*-di-*t*-butylbenzene, following the procedure of Kofod, Kumar and Sutton,<sup>189</sup> yielded a yellow solid. Fractional distillation gave some lower-boiling material, followed by a pale yellow oil, b.p. 106°/0.2 mm., which solidified on standing. Crystallisation (twice) from ethanol yielded colourless 1,4-dibromo-2,5-di-*t*-butylbenzene

(33%), m.p. 107-8° (lit.,<sup>189</sup> 107°).

N.m.r. ( $\text{CCl}_4$ ):  $\tau$  2.42 (s, 2H) and 8.51 (s, 18H, t-Bu).

D 2-Bromo-4-t-butylfluorobenzene

2-Bromo-4-t-butylacetanilide.— Bromination of p-t-butylacetanilide (19.1g., 0.10 mole) in acetic acid, by the method of Klouwen and Boelens,<sup>190</sup> gave a product which was found by g.l.c. examination (2% CAR, 200°) to contain ca. 30% unchanged starting material. A suspension of this product in acetic acid (50 ml.) was stirred vigorously at 60°, and a further portion of bromine (6.0g.) added during 1 hr. After 9 hr., no p-t-butylacetanilide could be detected (g.l.c.) in the reaction mixture, which was worked up as prescribed to yield, after crystallisation from ethanol-water (5:1), 2-bromo-4-t-butylacetanilide (23.6g., 0.088 mole, 88%), m.p. 160-61° (lit.,<sup>191</sup> 158°).

2-Bromo-4-t-butylbenzenediazonium Fluoroborate.— A mixture of 2-bromo-4-t-butylacetanilide (20.2g., 0.075 mole), hydrochloric acid (sp.gr. 1.16, 38 ml.) and water (35 ml.) was boiled under reflux in an atmosphere of nitrogen for 5 hr. The resulting solution was stirred vigorously and cooled in ice to give a suspension of fine crystals. Sodium nitrite (5.80g.) in water (19 ml.) was dripped in at 0° during 40 min., and then a cold, filtered, solution of sodium fluoroborate (13.8g.) in water (35 ml.) was added,



with vigorous stirring, during 5 min. After a further 40 min., the precipitate was collected on a filter, dried by suction, and dissolved in acetone (30 ml.). Addition of ether gave colourless plates of 2-bromo-4-t-butylbenzenediazonium fluoroborate (20.8g., 0.063 mole, 84%), m.p. 148-9° (decomp.).

2-Bromo-4-t-butylfluorobenzene.— This preparation was carried out under vacuum (ca. 1 mm.) in an apparatus set up for distillation. The receiver was immersed in a carbon tetrachloride slush-bath, and iced water circulated through the double-surface condenser. The experiment was conducted in an efficient fume-cupboard, into which the exhaust from the pump was fed.

The diazonium fluoroborate (20.7g., 0.063 mole) was heated gently with a small free flame, and a red liquid distilled over. When all the solid had decomposed, the flask was heated more strongly until no further distillate was collected. The crude material (13.3 g.) was redistilled to yield colourless 2-bromo-4-t-butylfluorobenzene (10.9g., 0.048 mole, 75%), b.p. 67-9°/2.05 mm. (Found: C, 51.6; H, 5.55.  $C_{10}H_{12}BrF$  requires C, 52.0; H, 5.2%).

N.m.r. (20% w/v in  $CCl_3F$ ):  $\tau$  2.48 (dd,  $H_3$ ), 2.76 (quartet of doublets,  $H_5$ ), 3.03 (dd appearing as a 1:2:1 triplet,  $H_6$ ) and

104.

8.70 (t-Bu).  $J_{3-5}$  2.4,  
 $J_{3-6}$  ca. 0.0,  $J_{5-6}$  9.0,  
 $J_{3-F}$  6.5,  $J_{5-F}$  4.6 and  
 $J_{6-F}$  9.0 c./sec.

$^{19}\text{F}$  n.m.r. (20% w/v in  $\text{CCl}_3\text{F}$ ) at 56.4 Mc./sec.: 112.5 parts per million upfield from  $\text{CCl}_3\text{F}$  (quartet of overlapping doublets).

I.r. (liquid): 1110  $\text{cm}^{-1}$  (C-F). Weak absorptions at 1885, 1825 and 1760  $\text{cm}^{-1}$  with positions and relative intensities expected of a 1,2,4-trisubstituted benzene.<sup>187</sup>

#### E 4-t-Butylanthranilic Acid

This synthesis was based on the experiments of Skinner and Zell.<sup>192</sup>

4-t-Butyl-2-nitrobenzoic Acid.— p-t-Butylbenzyl chloride (128g., 0.70 mole) was nitrated by the method of Nelson and Brown<sup>159</sup> for the nitration of t-butylbenzene. The crude product was fractionally distilled through a Vigreux column in an atmosphere of nitrogen, yielding lower-boiling material followed by a viscous orange oil (137.4g.), b.p. 107–18°/0.1 mm. Examination by g.l.c. (2% NPGS, 180°) revealed two partially resolved components, A (retention time 4.6 min., 70–80%) and B (5.2 min., 20–30%).



N.m.r. ( $\text{CCl}_4$ ):  $\tau$  1.96, 2.36, 2.50 and 2.69 (all multiplets, total 3H); 5.10 and 5.48 (singlets, total 2H, ratio 3.5:1); 8.62 (s, t-Bu).

The product appeared to be a mixture of 4-t-butyl-2-nitrobenzyl chloride (A) and 4-t-butyl-3-nitrobenzyl chloride (B) (total 0.61 mole, 86%).

The isomeric mixture (125g., 0.55 mole) was oxidised with alkaline potassium permanganate as described by Skinner and Zell<sup>192</sup> to yield, after repeated crystallisation from benzene-petroleum and from carbon tetrachloride, pale pink 4-t-butyl-2-nitrobenzoic acid (23.1g., 0.0104 mole, 19%), m.p. 152-4° (lit.,<sup>192</sup> 138-43°). Additional recrystallisations did not alter the melting point.

N.m.r. ( $\text{CCl}_4$ - $\text{CDCl}_3$ , 4:1):  $\tau$  -2.64 (sharp s, 1H), 1.95 - 2.45 (complex, 3H) and 8.60 (t-Bu).

4-t-Butylanthranilic Acid.— The nitro-acid (10.05g., 0.045 mole) in super-dry ethanol (185 ml.) was shaken at room temperature with platinum dioxide (Adams catalyst, 0.49g.) in an atmosphere of hydrogen. After  $2\frac{1}{2}$  hr., 3 l. of hydrogen had been consumed, and no further uptake occurred. The mixture was cautiously filtered, the filtrate concentrated to 40 ml., heated to boiling, and water (15 ml.) added. The pale yellow crystals that formed were recrystallised from

aqueous ethanol to yield 4-t-butylanthranilic acid (6.02g., 0.031 mole, 69%), m.p. 166-8° (lit.,<sup>192</sup> 167-8°).

I.r. (Nujol): 3510 and 3390 (NH<sub>2</sub>); 3500-2000 (broad, O-H); and 1670 cm.<sup>-1</sup> (C=O).

#### F 3-Chloroanthranilic Acid

This synthesis was based on the experiments of Holt and Saddler,<sup>193</sup> and Marvel and Hiers.<sup>194</sup>

2-Chloroisonitrosoacetanilide.-- Chloral hydrate (90.0g.) and water (1.2 l.) were vigorously stirred while the following reagents were added in order: sodium sulphate decahydrate (1300g.), a solution of freshly distilled o-chloroaniline (64.0g., 0.50 mole) in water (600 ml.) containing hydrochloric acid (sp.gr. 1.16, 51.2g.), and a solution of hydroxylamine hydrochloride (110g.) in water (500 ml.). The mixture was heated slowly to boiling, stirred under reflux for 50 min., and cooled to 12°. The solid matter, which contained much sodium sulphate, was filtered off and dissolved in warm water (2 l.), and the solution refrigerated overnight. The resulting precipitate was collected and stirred with warm 2N-sodium hydroxide solution (800 ml.), and the mixture filtered through 'Hyflo-Supercel'. The filter cake was washed with warm alkali (2 x 50 ml.) and the combined filtrates were swirled while 2N- hydrochloric acid was added until the mixture was acidic. The copious white precipitate was crystallised from ethanol-water (3:2) to yield 2-chloroiso-

nitrosoacetanilide (72.0g., 0.36 mole, 72%), m.p. 148-52° (lit.,<sup>193</sup> 152°).

7-Chloroisatin.— Sulphuric acid (sp.gr. 1.84, 515g.) was heated to 68° and the source of heat removed. Dry 2-chloroisonitrosoacetanilide (69.5g., 0.35 mole) was added in portions during 40 min. to the vigorously stirred acid, occasional cooling of the reaction vessel being necessary to prevent the temperature rising above 80°. When addition was complete, the mixture was heated at 80° for 12 min., allowed to cool to room temperature, and was poured into agitated iced water (4 l.). After 30 min. the resulting sludge was filtered off, washed with water, and stirred with 1N-sodium hydroxide solution (1 l.) at 100°. The source of heat was removed and glacial acetic acid slowly and cautiously added until the mixture was faintly acidic. Decolourising charcoal (8.0g.) was added, the mixture stirred at 100° for 10 min., and filtered through 'Hyflo-Supercel'. Hydrochloric acid (sp.gr. 1.16, 200 ml.) was added to the filtrate which yielded, when cold, orange crystals of 7-chloroisatin (32.8g., 0.18 mole, 51%), m.p. 181-2° (lit.,<sup>193</sup> 175°).

3-Chloroanthranilic Acid.— 7-Chloroisatin (25.7g., 0.14 mole) was dissolved in 1N-sodium hydroxide solution (450 ml.) and hydrogen peroxide (100 volume, 49.7 ml.)

dripped into the hot, stirred, solution during 10 min.

A sample removed after a further 5 min. did not turn orange when acidified. The solution was cooled and 0.5N-hydrochloric acid added until a permanent precipitate began to form.

Decolourising charcoal (5.0g.) was added, the mixture stirred and heated for 10 min., and filtered. 2N-Hydrochloric acid was added to the filtrate until precipitation was complete, and the flocculent solid was collected on a filter and washed with water. Crystallisation from ethanol-water (2:3) yielded pale brown 3-chloroanthranilic acid (21.6g., 0.13 mole, 89%), m.p. 190-92° (lit.,<sup>193</sup> 192°).

I.r. (Nujol): 3480 and 3360 (N-H); 1665 cm.<sup>-1</sup> (C=O).

#### G Benzyne precursors

Anthranilic acid was crystallised from benzene containing a little ethanol, and had m.p. 145-6° (lit.,<sup>169</sup> 144-6°).

o-Dibromobenzene was distilled from phosphorus pentoxide, b.p. 92-4°/10 mm.

### VI PREPARATION OF ARYNE ADDUCTS

All the following reactions were carried out under anhydrous conditions in an atmosphere of oxygen-free nitrogen.

A 6-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide

From 4-t-Butylanthranilic Acid.— A mixture of pentyl nitrite (2.93g.), furan (6.80g.) and dichloromethane (70 ml.) was stirred and boiled under reflux while a solution of 4-t-butylanthranilic acid (3.86g., 0.020 mole) in acetone (20 ml.) was dripped in during 4 hr. After boiling for a further 2 hr. the mixture was fractionally distilled to yield pale yellow 6-t-butyl-1,4-dihydronaphthalene-1,4-endoxide (1.01g., 0.005 mole, 25%), b.p.  $83-4^{\circ}/0.04$  mm. (Found: C, 83.9; H, 7.9.  $C_{14}H_{16}O$  requires C, 84.0; H, 8.05%).

N.m.r. spectrum: see Appendix.

I.r. (liquid): 1390 and 1360 (t-Bu); 1155 (C-O-C) and  $700\text{ cm.}^{-1}$  (cis CH=CH).

Mass spectrum: Parent ion, m/e 200.  $C_{14}H_{16}O$  requires  $M = 200$ .

$M + 1/M = 17.0\%$ .  $C_{14}H_{16}O$  requires

$M + 1/M = 15.42\%$

$M + 2/M = 1.8\%$ .  $C_{14}H_{16}O$  requires

$M + 2/M = 1.31\%$ .

Metastable peaks at 171, 133 and 105.

Attempted Preparation of 6-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide from Other Sources of 4-t-Butylbenzyne.— Generation of 4-t-butylbenzyne from 2-bromo-4-t-butylfluorobenzene with lithium amalgam<sup>65</sup> in the presence of furan gave 2-t-butyl-naphthalene as the only isolable product. This aryne

precursor reacted with butyl-lithium<sup>62</sup> in furan to give a mixture of products (g.l.c.). Distillation afforded a pale yellow oil, b.p. 52-130°/0.04 mm.; the i.r. spectrum contained a broad band at 3430 cm.<sup>-1</sup> (O-H). All attempts to prepare the Grignard reagent,<sup>65,87</sup> and hence 4-t-butylbenzyne, from 2-bromo-4-t-butylfluorobenzene were unsuccessful.

p-Bromo-t-butylbenzene was heated with potassium t-butoxide in dimethyl sulphoxide<sup>57</sup> containing furan. G.l.c. examination of the reaction mixture indicated that very little dehydrobromination had occurred after 37 hr. at 70°.

B 6-t-Butyl-1,2,3,4-tetraphenylnaphthalene

A mixture of pentyl nitrite (0.70g.), 2,3,4,5-tetraphenylcyclopentadienone (2.30g.) and dichloromethane (20 ml.) was stirred and boiled under reflux. A solution of 4-t-butylanthranilic acid (0.97g., 5.0 mmoles) in acetone (6 ml.) was dripped in during 4 hr. and the mixture was boiled for a further 2 hr. Volatile material was removed by evaporation under reduced pressure, and the residue was chromatographed on alumina (350g.). Elution with petroleum-benzene (4:1) gave a white solid (1.40g.) which was crystallised from benzene-methanol to yield colourless 6-t-butyl-1,2,3,4-tetraphenylnaphthalene (1.16g., 2.39 mmoles, 48%), m.p. 286-7°. This material was identical (m.p., mixed m.p., and i.r. and n.m.r. spectra) to the adduct isolated from the reaction of



p-t-butyl-N-nitrosoacetanilide with 2,3,4,5-tetraphenyl-cyclopentadienone (p. 143).

C 1-(p-t-Butylphenyl)-2,3,4-triphenylnaphthalene

Anthranilic acid (1.37g., 10.0 mmoles) was diazotised with pentyl nitrite in the presence of 2-(p-t-butylphenyl)-3,4,5-triphenylcyclopentadienone (4.41g.) as described above. Chromatography of the reaction product on alumina (500g.) afforded, by elution with petroleum-benzene (6:1), a colourless solid (3.98g.) which was crystallised from acetic acid and from benzene-methanol (1:1) to yield 1-(p-t-butylphenyl)-2,3,4-triphenylnaphthalene (3.41g., 7.00 mmoles, 70%), m.p. 200-201°. (Found: C, 93.0; H, 6.7.  $C_{38}H_{32}$  requires C, 93.4; H, 6.6%). N.m.r. spectrum: see Appendix.

I.r. (Nujol): 1070, 1025, 845, 770, 755, 700, 685 and 655  $cm^{-1}$ .

D 5-Chloro-1,2,3,4-tetraphenylnaphthalene

Diazotisation of 3-chloroanthranilic acid (1.75g., 10.2 mmoles) with pentyl nitrite in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (5.76g.) in dichloromethane, as in the preceding experiments, gave a product which was chromatographed on alumina (220g.). Elution with petroleum-benzene (1:1) afforded a white solid (0.508g.) which, crystallised from benzene-methanol (3:2), gave 5-chloro-1,2,3,4-tetraphenylnaphthalene (0.355g., 0.76 mmole, 7.5%; crude 10.6%), m.p. 256.5-7.5°. (Found: C, 87.2; H, 5.2;

Cl, 7.3.  $C_{34}H_{23}Cl$  requires C, 87.4; H, 5.0; Cl, 7.6%.

N.m.r. spectrum: see Appendix.

$\lambda_{max.}$  ( $\log \epsilon$ ) in cyclohexane: 220(4.65), 242(4.68), 247(4.71),  
250(4.68), 255(4.56), 282(4.15)  
and 306 m $\mu$  (4.09).

E Adduct of 3-Chlorobenzynes with Phenyl Azide

A solution of 3-chloroanthranilic acid (5.21g., 30.4 mmole s) in acetone (60 ml.) and benzene (40 ml.) was added dropwise during 4 hr. to a stirred mixture of pentyl nitrite (3.90g.), phenyl azide (5.36g.) and benzene (120 ml.) at 60°. After heating for a further 1 hr. at 62°, volatile material was evaporated under reduced pressure and the residue chromatographed on alumina (200g.). Elution with benzene-ether (20:1) gave a pale yellow solid (0.383g.), which appeared from g.l.c. examination (1% APL, 220°) to be a single compound. Crystallisation from petroleum-benzene yielded colourless needles of 4- and/or 7-chloro-1-phenylbenzotriazole (0.244g., 1.06 mmole s, 3.5%; crude 5.5%) m.p. 115-6°. (Found: C, 62.8; H, 3.4.

$C_{12}H_8N_3Cl$  requires C, 62.75; H, 3.5%). After fusion with sodium, a sample of this material gave positive tests for halogen and nitrogen.

N.m.r. ( $CDCl_3$ ):  $\tau$  2.00-2.73 (very complex).

$\lambda_{max.}$  ( $\log \epsilon$ ) in ethanol: 235(4.11), 253.5(3.76), 260sh(3.83),  
264.5(3.88), 272(3.88) and  
296 m $\mu$ (3.88).



It was not possible to establish whether this product was 4- or 7-chloro-1-phenylbenzotriazole, or a mixture of isomers.

Elution with solvents of increasing polarity gave no further tractable fractions. The column packing was extracted with hot acetic acid and the cooled extract filtered, evaporated to dryness, and dissolved in chloroform. Extraction with alkali and acidification of the extracts gave a precipitate which, crystallised from ethanol-water, yielded 3-chloroanthranilic acid (2.06g., 12.0 mmoles), identified by its m.p., mixed m.p. and i.r. spectrum. Based on the amount of aryne precursor consumed (18.4 mmoles), the yield of adduct was 5.8%; crude 9.1%.

#### F 1-Phenylbenzotriazole

An experiment similar to that described above, but using unsubstituted anthranilic acid, yielded 1-phenylbenzotriazole (55%; crude 58%), m.p. 87-8° (lit.,<sup>101</sup> 89-90°).

N.m.r. (CDCl<sub>3</sub>):  $\tau$  1.70-2.85 (very complex).

$\lambda_{\max.}$  (log  $\epsilon$ ) in ethanol: 236.5(4.10), 260(3.94), 266sh(3.91)  
and 292.5 m $\mu$ (3.83).

#### G 1,4-Dimethyl-1,4-dihydronaphthalene-1,4-endoxide<sup>86</sup>

A solution of butyl-lithium in ether, prepared from 1-bromobutane (3.42g., 0.025 mole) by the method of Vogel,<sup>158</sup> was filtered in a stream of nitrogen through a glass-wool plug, and diluted with ether (to 20 ml.). The filtrate was

stirred efficiently at  $-70^{\circ}$  while 2,5-dimethylfuran (5.76g.) was added during 10 min. A solution of o-dibromobenzene (4.72g., 0.020 mole) in ether (8 ml.) was introduced dropwise during 30 min. After a further 45 min. at  $-70^{\circ}$  the mixture was allowed to warm to room temperature, and stirring was continued for 2 hr. Ether (30 ml.) was added, and the mixture was poured into water (50 ml.), when heat was generated. The layers were separated, the aqueous portion was extracted with ether (2 x 15 ml.), and all the ether extracts were combined, washed with water, and dried over potassium carbonate. The yellow oil remaining after evaporation of volatile material was examined by g.l.c. (2% NPGS,  $103^{\circ}$ ) and found to contain much o-dibromobenzene, together with one other component. Repeated crystallisation from petroleum at  $-60^{\circ}$  yielded 1,4-dimethyl-1,4-dihydronaphthalene-1,4-endoxide (0.784g., 0.0046 mole, 23%), m.p.  $32-3^{\circ}$  (lit.,<sup>86</sup>  $35-35.5^{\circ}$ ).

N.m.r. ( $\text{CCl}_4$ ): see Appendix.

I.r. (melt): 1145 (C-O-C) and 700  $\text{cm}^{-1}$  (cis CH=CH).

H 6,13-Di-t-butyl-5,7,12,14-tetrahydro-5,14:7,12-di-o-benzeno-pentacene

A mixture of 1,4-dibromo-2,5-di-t-butylbenzene (7.41g., 21.3 mmoles), anthracene (9.20g.) and t-butylbenzene (35 ml.) was boiled under reflux, and potassium t-butoxide (5.29 g.) added in portions during 3 hr. After boiling for a

further 16 hr. unreacted anthracene was removed by adding maleic anhydride (5.70g.) and boiling for 30 min. The mixture was allowed to stand without heating for 2 hr., and was then boiled for 2.5 hr. with 8% sodium hydroxide solution (30 ml.). The cooled mixture was filtered, the solid exhaustively extracted with hot benzene to give a fluorescent solution, and the filtrate extracted with ether. The organic extracts were combined, dried over calcium sulphate, and evaporated to a yellow solid (8.97g.) which was chromatographed on alumina (700g.). Elution with petroleum gave a white solid (0.194g.), m.p. 188-90°, which from methanol yielded colourless needles (0.154g.), m.p. 189-90°. (Found: C, 78.65; H, 11.4%). This material appeared, by g.l.c. examination (CAR capillary, 160°), to be a single compound.

N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  2.91 (s, 2H), 8.48 (s, 18H, t-BuO) and 8.62 (s, 18H, t-Bu).

I.r. (Nujol): small bands at 1805 and 1715  $\text{cm}^{-1}$ , the latter being rather more intense, consistent with a 1,2,4,5-tetrasubstituted benzene.<sup>187</sup>

This product was probably 1,4-di-t-butoxy-2,5-di-t-butylbenzene (2.2%). ( $\text{C}_{22}\text{H}_{38}\text{O}_2$  requires C, 79.0; H, 11.45%).

Elution with petroleum-benzene (10:1) gave a white solid (0.290g.) which was crystallised (twice) from benzene-methanol to yield 1,4-di-t-butyltriptycene (0.141g., 0.39 mmole, 1.8%),

m.p. 230-32°, mixed m.p. 232-4°. The n.m.r. and i.r. spectra were identical to those of the adduct from the reaction of 2,5-di-*t*-butyl-*N*-nitrosoacetanilide with anthracene (p.161).

Elution with petroleum-benzene (1:1) gave a white solid (0.428g.) which from benzene-methanol formed needles of 6,13-di-*t*-butyl-5,7,12,14-tetrahydro-5,14:7,12-di-*o*-benzeno-pentacene (0.234g., 0.43 mmole, 2.0%; crude, 3.7%), m.p. 380-83°. (Found: C, 92.8; H, 7.15.  $C_{42}H_{38}$  requires C, 92.9; H, 7.1%).

N.m.r. ( $CDCl_3$ ):  $\tau$  2.86 (centre of AA'BB', 16H), 3.82(s, 4H, bridge-head), and 8.12 (s, 18H, *t*-Bu).

$\lambda_{max}$ . (methanol): 210, 234, 262.5, 280 and 305 m $\mu$ .

I Attempted Preparation of 5,10-Di-*t*-butyl-1,4,6,9-tetrahydroanthracene-1,4:6,9-diendoxide

1,4-Dibromo-2,5-di-*t*-butylbenzene (7.12g., 26.2 mmoles) and furan (14.2g.) in dimethyl sulfoxide (40 ml.) were stirred at 60° while a solution of potassium *t*-butoxide (5.87g.) in dimethyl sulfoxide (40 ml.) was added during 5.5 hr. Heating was continued for a further 10.5 hr., and an additional portion (1.05g.) of potassium *t*-butoxide added. After a further 3 hr. at 60°, volatile material was removed under vacuum, and ether and water were added to the residue. The layers were separated, the aqueous portion was extracted with ether, and the combined ethereal

extracts were dried over calcium sulphate. Evaporation of the solvent left a yellow solid (9.72g.), the bulk (6.30g.) of which was chromatographed on silica gel (500g.). Elution with benzene gave a white solid (2.54g.) which from g.l.c. examination (2% NPGS and 3% APL, 225°) appeared to be a single compound. Crystallisation from light-petroleum (b.p. 60-80°) afforded 2-bromo-1,4-di-*t*-butyl-5,8-dihydro-naphthalene-5,8-endoxide (1.91g., 5.69 mmoles, 33.5%; crude, 44.5%), m.p. 149-51°. (Found: C, 64.2; H, 6.8; Br, 23.9.  $C_{18}H_{23}BrO$  requires C, 64.5; H, 6.9; Br, 23.8%).

N.m.r. spectrum: see Appendix.

I.r. (Nujol): 1120 (C-O-C) and 730  $cm^{-1}$  (cis CH=CH).

No other identifiable product was isolated.

A sample of the endoxide was heated with potassium *t*-butoxide, furan, and dimethyl sulphoxide under conditions similar to those described above. The reaction mixture was examined by g.l.c. (2% NPGS, 225°) after 26 hr., and was found to contain most of the starting material unchanged.

#### J 1,4-Dihydronaphthalene-1,4-endoxide

1,4-Dihydronaphthalene-1,4-endoxide, prepared by Dr. J.T. Sharp, was crystallised from petroleum and had m.p. 55-6° (lit.,<sup>65</sup> 55-6°).

## VII PREPARATION OF ACETYLARYLNITROSAMINES

Acetylarylnitrosamines were prepared by methods based on the experiments of France, Heilbron and Hey,<sup>195</sup> and Miles and Suschitzky.<sup>142a</sup> No attempt was made to purify, or obtain elemental analysis of, any of these unstable compounds.

### A Solid Acetylarylnitrosamines

o-t-Butyl-N-nitrosoacetanilide.— A suspension of o-t-butylacetanilide (11.8g., 0.062 mole) in a mixture of glacial acetic acid (37g.), acetic anhydride (38g.) and pyridine (2 ml.) was stirred at 0° under anhydrous conditions. Nitrosyl chloride (6.8g., 0.104 mole), as a 30% solution in acetic anhydride, was added dropwise during 30 min., and stirring continued for a further 2 hr. The solution was poured into agitated iced water (1.6 l.) and the precipitated yellow solid was collected on a filter, washed with ice-cold water and 10% potassium hydrogen carbonate solution, and dried at the pump. After pressing between sheets of filter paper, the solid was dried over phosphorus pentoxide and potassium hydroxide pellets at 0.05 mm. for 2 hr. to give o-t-butyl-N-nitrosoacetanilide (12.1g., 0.055 mole, 90%), m.p. 60° (decomp.); lit.,<sup>153</sup> m.p. 62° (decomp.).

I.r. (Nujol): 1740 cm.<sup>-1</sup> (C=O). No absorption at 3250 cm.<sup>-1</sup>

(N-H in the amide).

N.m.r. (benzene):  $\tau$  7.52 (Me) and 8.94 (t-Bu).



The following nitrosamides were prepared similarly.

In each case the i.r. spectrum (Nujol) contained a C=O absorption (1750-1725  $\text{cm}^{-1}$ ) at a higher frequency than in the corresponding amide (1690-1640  $\text{cm}^{-1}$ ); and the absence of an N-H absorption (3400-3000  $\text{cm}^{-1}$ ) was an indication of the complete conversion of the amide.

p-t-Butyl-N-nitrosoacetanilide.- (86% Yield),

m.p. 40° (decomp.); lit.,<sup>153</sup> m.p. 57.5° (decomp.).

One sample of this compound exploded after 4 hr. at room temperature.

o-t-Butyl-N-nitroso-2,2,2-trideuterioacetanilide.-

(94% Yield), m.p. 65° (decomp.).

N.m.r. (benzene):  $\tau$  8.95 (t-Bu); no absorption at 7.52.

p-t-Butyl-N-nitroso-2,2,2-trideuterioacetanilide.-

(85% Yield), m.p. 45° (decomp.).

N.m.r. (benzene):  $\tau$  8.90 (t-Bu); no absorption at 7-8.

2,5-Di-t-butyl-N-nitrosoacetanilide.- (96% Yield),

m.p. 66-8° (decomp.).

4-Acetoxy-2,5-di-t-butyl-N-nitrosoacetanilide.- (94% Yield)

m.p. 110° (decomp.).

N-Nitrosoacetanilide.- (73% Yield), m.p. 50° (decomp.);

lit.,<sup>195</sup> m.p. 50° (decomp.).

p-Acetoxy-N-nitrosoacetanilide.- (65% Yield)

m.p. 74° (decomp.).

o-Chloro-N-nitrosoacetanilide.-- (82% Yield),

m.p. 46-7° (decomp.); lit., m.p. 59° (decomp.),<sup>196</sup>

46-7° (decomp.),<sup>155</sup>

p-Chloro-N-nitrosoacetanilide.-- (88% Yield),

m.p. 71° (decomp.); lit.,<sup>142a</sup> m.p. 77° (decomp.).

## B Liquid Acetylarlylnitrosamines

The following compounds were yellow oils, and were prepared essentially as above, except for the method of isolation which is described for each reaction of each nitrosamide (Section IX).

m-t-Butyl-N-nitrosoacetanilide.--

I.r. ( $\text{CCl}_4$ , 0.2 mm. AgCl cell): 1740  $\text{cm}^{-1}$  (C=O).

No absorption at 3330-3090  $\text{cm}^{-1}$  (N-H in the amide).

m-Chloro-N-nitrosoacetanilide.

Diphenyl [o-(N-nitrosoacetamido)phenyl] phosphine Oxide.--

I.r. ( $\text{CCl}_4$ , 0.2 mm. AgCl cell): 1740  $\text{cm}^{-1}$  (C=O).

An absorption of similar intensity at 1715  $\text{cm}^{-1}$

(C=O in the amide) indicated that nitrosation was not complete.

2,5-Di-t-butyl-1,3-di-(N-nitrosoacetamido)benzene.--

3.3 Moles of nitrosyl chloride per mole of diamide were used.

## C Special Methods

Diethyl o-(N-Nitrosoacetamido)phenylphosphonate.-- A mixture of diethyl o-acetamidophenylphosphonate (1.37g.,



5.00 mmoles), fused potassium acetate (0.74g.), phosphorus pentoxide (0.07g.), acetic acid (3.0g.) and acetic anhydride (3.1g.) was stirred at 0° while nitrosyl chloride (0.49g., 7.50 mmoles), as 30% solution in acetic anhydride, was dripped in during 15 min. The mixture was stirred at 0° for a further 6 hr., poured into iced water (60 ml.), and the resulting oil extracted with benzene (15, 3 x 5 ml.). The combined extracts were washed with 10% potassium hydrogen carbonate solution (20 ml.) and water (2 x 15 ml.), and dried by stirring with magnesium sulphate for 20 min. and phosphorus pentoxide for 5 min. Solid material was filtered off and the filtrate evaporated at room temperature under reduced pressure to a brown oil, which was pumped at 0.1 mm. for 2 hr. to yield diethyl o-(N-nitrosoacetamido)phenylphosphonate (1.42g., 4.74 mmoles, 95%).

I.r. (liquid): 1735 cm.<sup>-1</sup> (C=O). No absorption at 3310-3120 cm.<sup>-1</sup> (N-H in the amide).

1,4-Di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene. (a) A suspension of (highly insoluble) 1,4-diacetamido-2,5-di-*t*-butylbenzene (3.60g., 0.012 mole) in acetic acid and acetic anhydride was treated with nitrosyl chloride (3.60g., 0.055 mole) as described for the nitrosation of o-*t*-butylacetanilide. After very efficient stirring at room temperature for 22 hr., a yellow powder (3.16g.), m.p. 105° (decomp.) was obtained.

The i.r. spectrum contained an absorption at  $1750\text{ cm.}^{-1}$  ( $\text{C=O}$ ), but also bands of appreciable intensity at  $3290$  and  $1660\text{ cm.}^{-1}$  ( $\text{N-H}$  and  $\text{C=O}$  in the amide) indicating that nitrosation was only ca. 90% complete.

(b) 2,5-Di-*t*-butyl-*p*-phenylenediamine (10.5g., 0.048 mole) was stirred in a dry flask at  $0^{\circ}$ , and a cold mixture of acetic acid (66g.), acetic anhydride (105g.), and pyridine (16 ml.) added. Dropwise addition of nitrosyl chloride (12.2g., 0.186 mole), as a 30% solution in acetic anhydride, was commenced immediately and completed within 20 min. After stirring for 2.5 hr. the mixture was poured into agitated iced water (800 ml.) and the precipitate collected on a filter, washed with water, pressed between sheets of filter paper, and dried over phosphorus pentoxide at 0.2 mm. for 4 hr. The dry dinitrosamide (16.1g., 0.0445 mole, 93%) had m.p.  $106^{\circ}$  (decomp.); its i.r. spectrum contained bands at 1755 and  $1740\text{ cm.}^{-1}$  ( $\text{C=O}$ ), but not at  $3290$  or  $1660\text{ cm.}^{-1}$  [This spectrum was obtained under higher resolution than that in (a) above]

#### VIII MISCELLANEOUS REACTIONS

##### A Preparation of *p*-Di-*t*-butylbenzene

Alkylation of *t*-butylbenzene with freshly prepared *t*-butyl chloride (b.p.  $51.5^{\circ}$ ) following the procedure of

Cadogan, Hey and Williams,<sup>153</sup> gave p-di-t-butylbenzene (56%), m.p. 77-8° (lit.,<sup>153</sup> 76-7°).

#### B Preparation of p-t-Butylbenzyl Chloride

This preparation, basically the method of Klouwen and Boelens,<sup>190</sup> was carried out under anhydrous conditions.

t-Butylbenzene (241g., 1.80 moles) was stirred with powdered anhydrous zinc chloride (26g.) and paraformaldehyde (40g.). A rapid stream of dry hydrogen chloride was passed through the mixture, which was slowly heated to 60°. After 8 hr. a further portion (6g.) of zinc chloride was added, the temperature raised to 80°, and heating continued for a further 2 hr. Benzene (500 ml.) and water (300 ml.) were added to the cooled mixture, sodium sulphate was added to break the emulsion, and the layers were separated. The organic portion was washed with water (2 x 200 ml.), 5% potassium hydrogen carbonate solution (200 ml.) and water (3 x 200 ml.), and dried over calcium chloride. Fractional distillation through a vacuum-jacketed Vigreux column yielded p-t-butylbenzyl chloride (171g., 0.94 mole, 52%), b.p. 124-8°/14 mm.

N.m.r. (CCl<sub>4</sub>):  $\tau$  2.71 (s, 4H), 5.53 (-CH<sub>2</sub>-) and 8.70 (t-Bu).

#### C Preparation of Nitrosyl Chloride

Nitrosyl chloride was prepared by the method of Morton and Wilcox,<sup>197</sup> by allowing an aqueous solution of sodium nitrite to react with hydrochloric acid. The product was dissolved

in acetic anhydride to give a 30% w/v solution which was stored at  $-10^{\circ}$ .

#### D Preparation of Lithium Amalgam

Lithium was heated with mercury, as described by Wittig and Pohmer,<sup>65</sup> in a quartz vessel through which a stream of dry helium was passed.

#### E Preparation of "Galvinoxyl"

##### 4,4'-Dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenylmethane.

This compound was prepared in low yield, following the procedure of Kharasch and Joshi,<sup>198</sup> from 2,6-di-*t*-butylphenol and formaldehyde. The product, after crystallisation from ethanol, had m.p.  $156-7^{\circ}$  (lit.,  $157^{\circ}$ ).

"Galvinoxyl":- The dihydroxy compound was oxidised with lead peroxide, and the product purified, as described by Bartlett and Funahashi.<sup>17</sup> After crystallisation from ethanol, deep blue "Galvinoxyl" (62%), m.p.  $153-4^{\circ}$  (lit.,<sup>17</sup>  $153.2-3.6^{\circ}$ ) was obtained.

#### F Preparation of Ethyl Nitrite and Pentyl Nitrite

Alkyl nitrites were prepared from the corresponding alcohols, following the general procedure of Noyes.<sup>199</sup> Pentyl nitrite was distilled, b.p.  $103-5^{\circ}$ ; ethyl nitrite was volatalised into a cold trap; both compounds were dried over molecular sieve, stored at  $-10^{\circ}$ , and redistilled immediately before use.

G Reaction of o-Bromo-t-butylbenzene with Sodamide

Liquid ammonia (50 ml.) was stirred in a flask fitted with an air-condenser surrounded by solid carbon dioxide, and protected by a soda-lime guard tube. The flask was immersed in a bath at  $-35^{\circ}$ , and small pieces of sodium were added until the ammonia acquired a permanent blue colour. A few small crystals of hydrated ferric nitrate were added, and the colour was discharged. Sodium (0.92g., 0.040g.atom) was introduced in four pieces at intervals of 5 min. When no blue colouration remained, o-bromo-t-butylbenzene (2.07g., 0.0097 mole) was run rapidly into the grey suspension, and vigorous stirring continued for 1.5 hr. Ammonium chloride (2.68g., 0.050 mole) was cautiously added in small portions and the system diluted with ether (50 ml.) and stirred until all the ammonia had evaporated. Water (100 ml.) was added, the layers were separated, the aqueous portion was extracted with ether (2 x 50 ml.), and the combined ethereal extracts were washed, and dried over magnesium sulphate.

A sample of the yellow solution was examined by g.l.c. (10% CAR,  $159^{\circ}$ ) with naphthalene as internal standard, and was found to contain m-t-butylaniline (27.3 moles/100 moles aryl halide). o-t-Butylaniline (0.38 mole/100 moles aryl halide would have been detected) was absent, and no starting material remained.

## IX REACTIONS OF ACETYLARYLNITROSAMINES

### A General Technique

All reactions were stirred under anhydrous conditions in an atmosphere of oxygen-free nitrogen for 14-16 hr. at room temperature, or as stated. To ensure complete decomposition of the nitrosamide, the reaction mixture was heated slowly to the reflux temperature, and boiled for 1 hr. Measured fractions of the reaction mixture were withdrawn for examination by g.l.c. or in other ways. In general, structural assignments based solely on g.l.c. retention times were the result of analysis on at least two different stationary phases. In all cases, the relation of a peak in the chromatogram to a particular compound required that the peak be enhanced, relative to other peaks, when authentic material was added to the reaction mixture.

The yield of acetic acid could be determined by g.l.c. (CAR) using the D.6 instrument, or more accurately, by treating a (measured) sample of the reaction mixture with an excess of sodium hydroxide solution, and back-titrating the excess of alkali against standard hydrochloric acid, with phenolphthalein as indicator.

The yields of decomposition products are quoted in moles per 100 moles of nitrosamide (or dinitrosamide), i.e. m/100 m.

Literature values of physical constants quoted for authentic specimens prepared in preceding sections are not repeated in this section.



B Reactions of o-, m-, and p-Chloro-N-nitrosoacetanilides

1. Reaction of o-Chloro-N-nitrosoacetanilide with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene

The nitrosamide (7.01g., 35.3 mmoles) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (13.5g., 35.1 mmoles) in benzene (81.9g., 1.05 moles) at 38° for 15 hr. and at the reflux temperature for 1 hr. The cooled reaction mixture was filtered, the solid washed with benzene, and a portion of the combined filtrate and washings examined by g.l.c. (10% CAR, 198°; 2% NPGS, 130°; 10% SIL, 70° and 200°) with biphenyl as internal standard. The following products were detected: acetic acid (35m/100m), chlorobenzene (0.5), o-chlorophenyl acetate (0.4), 2-chlorobiphenyl (28.4), 2-acetoxibiphenyl (3.9) and o-chloroacetanilide (6.0). m- and p-Chlorophenyl acetates (0.02m/100m would have been detected) were absent.

The major part (33.3 mmoles nitrosamide) of the filtrate and all the solid material were chromatographed on alumina (1250g.). Elution with petroleum containing benzene (1-5%) yielded colourless 2-chlorobiphenyl (crude, 1.55g., 8.19 mmoles, 24.6m/100m); m.p. 31-31.5°, mixed m.p. 30-31.5°, after crystallisation from petroleum at -40°. The i.r. spectrum was identical to that of the authentic material. Further fractions, eluted with solvents of

steadily increasing polarity, were examined by t.l.c., and i.r. and u.v. spectroscopy. No 5-chloro-1,2,3,4-tetraphenyl-naphthalene was detected.

2,3,4,5-Tetraphenylcyclopentadienone (8.90g., 23.2 mmols) was eluted in benzene.

2. Reaction of p-Chloro-N-nitrosoacetanilide with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene

p-Chloro-N-nitrosoacetanilide (7.98g., 40.2 mmols) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (15.3g., 39.8 mmols) in benzene (93.6g., 1.20 moles). The cooled reaction mixture was filtered, the solid matter washed with benzene, and the bulk (36.2 mmols nitrosamide) of the filtrate and washings, together with all the solid, was chromatographed on alumina (600g.). Elution with petroleum-benzene (3:7) yielded 4-chlorobiphenyl (crude, 0.358g., 1.90 mmols, 5.25m/100m); m.p. and mixed m.p. 75-6° after crystallisation from petroleum. The i.r. spectrum was indistinguishable from that of the authentic biaryl.

Elution with petroleum-benzene (2:8) gave a white solid (0.729g.) which was crystallised from acetic acid to yield 6-chloro-1,2,3,4-tetraphenylnaphthalene (0.449g., 0.96 mmole, 2.7m/100m), m.p. 229-9.5°. (Found: C, 87.25; H, 5.05.

$C_{34}H_{23}Cl$  requires C, 87.4; H, 5.0%).



N.m.r. spectrum: see Appendix.

$\lambda_{\text{max.}}(\log \epsilon)$  in hexane: 226(4.60), 242(4.72), 247(4.77),  
251(4.73), 257(4.60), 278sh(4.24)  
and 297.5m $\mu$ (4.11).

I.r. (Nujol): 1603, 742 and 700 cm.<sup>-1</sup> Weaker bands include 894  
and 877 cm.<sup>-1</sup>

2,3,4,5-Tetraphenylcyclopentadienone (8.64g., 22.5 mmoles)  
was eluted in benzene.

A sample of the filtered reaction mixture was examined  
by g.l.c. (2% NPGS, 105° and 195°). The yields of the  
products detected were estimated by assuming the yield of  
4-chlorobiphenyl to be that in which it was isolated, and  
using this as an internal standard: p-chlorophenyl acetate  
(0.9m/100m), 4-acetoxibiphenyl (0.6) and p-chloroacetanilide  
(0.8). o- and m-Chlorophenyl acetates (0.05m/100m would  
have been detected) were absent.

### 3. Reaction of m-Chloro-N-nitrosoacetanilide with 2,3,4,5- Tetraphenylcyclopentadienone in Benzene

m-Chloroacetanilide (6.785g., 40.0 mmoles) was nitrosated  
and the yellow oil which separated when the reaction mixture  
was poured into iced water (700 ml.) was extracted with  
benzene (90, 20 ml.). The combined extracts were washed  
with 5% sodium carbonate solution (100 ml.) and water  
(200 ml.) and dried over calcium chloride for 20 min., the

temperature being kept below  $5^{\circ}$ . The solid material was filtered off and washed with benzene, and the filtrate, containing the nitrosamide (assumed 40.0 mmoles) in benzene (140 ml.) was stirred with 2,3,4,5-tetraphenylcyclopentadione (15.3g., 39.9 mmoles). When the reaction was complete, the mixture was filtered, the solid matter washed with benzene, and the bulk (34.8 mmoles nitrosamide) of the filtrate, together with all the solid, was chromatographed on alumina (580g.). Elution with petroleum-benzene (3:2) gave colourless 3-chlorobiphenyl (crude, 0.182g., 0.97 mmole, 2.8m/100m), identified by comparison of its refractive index and i.r. spectrum with those of an authentic specimen.

Elution with petroleum-benzene (2:3) gave an oily white solid which was washed with very little cold petroleum to yield a powder (3.03g.), m.p.  $240-55^{\circ}$ . The i.r. spectrum was identical to that of authentic 5-chloro-1,2,3,4-tetraphenylnaphthalene (m.p.  $256.5-7.5^{\circ}$ ) and was distinguished from that of the 6-chloro-1,2,3,4-tetraphenylnaphthalene from B.2 (m.p.  $229-9.5^{\circ}$ ) by the absence of bands at 894, 877 and  $742\text{ cm.}^{-1}$ . The n.m.r. spectrum was identical to that of the 5-chloro compound. From acetic acid the powder gave crystals of 5-chloro-1,2,3,4-tetraphenylnaphthalene (2.27g., 4.86 mmoles, 14.0m/100m; crude, 18.8m/100m),

m.p. and mixed m.p. 255-6.5°. Other fractions were examined by t.l.c. and found to contain neither 5- nor 6-chloro-1,2,3,4-tetraphenylnaphthalene (which were not resolved). The yield of the 6-chloro compound was, therefore, not greater than 4.8m/100m; the i.r. spectrum of the crude adduct suggested a yield of less than 1.0m/100m.

2,3,4,5-Tetraphenylcyclopentadienone (10.4g., 27.0 mmoles) was eluted in benzene.

A sample of the filtered reaction mixture was examined by g.l.c. (2% NPGS, 105° and 195°), and the yields of the following products were computed by assuming the yield of 3-chlorobiphenyl to be that in which it was isolated: m-chlorophenyl acetate (0.5m/100m), 3-acetoxibiphenyl (0.1) and m-chloroacetanilide (7.8). o- and p-Chlorophenyl acetates (0.05m/100m would have been detected) were absent.

#### 4. Reaction of o-Chloro-N-nitrosoacetanilide with Phenyl Azide in Benzene

o-Chloro-N-nitrosoacetanilide (2.71g., 13.6 mmoles) was allowed to decompose in benzene (31.8g., 0.408 mole) containing phenyl azide (2.44g., 20.4 mmoles) at 40° for 16 hr. and at the reflux temperature for 1 hr. A sample of the resulting solution, examined by g.l.c. (10% CAR, 193°; 3% APL, 180°) with biphenyl as internal

standard was found to contain: 2-chlorobiphenyl (35.9m/100m) and o-chloroacetanilide (24.1). o-Chlorophenyl acetate (0.2m/100m would have been detected) and 2-acetoxybiphenyl (0.3) were absent.

Examination of the reaction mixture by t.l.c. on alumina did not reveal a component having an  $R_F$  value equal to that of the product from the reaction of phenyl azide with 3-chlorobenzene. G.l.c. examination (1% APL, 230°) confirmed the absence of the aryne adduct (0.05m/100m would have been detected).

The i.r. spectrum of the nitrosamide used in this experiment contained no absorption at 3240  $\text{cm}^{-1}$  (N-H in o-chloroacetanilide).

## C Reactions of N-Nitrosoacetanilide

### 1. Reaction with Phenyl Azide in Benzene

N-Nitrosoacetanilide (4.11g., 25.0 mmoles) was allowed to decompose in benzene (58.5g., 0.75 mole) containing phenyl azide (4.45g., 37.5 mmoles) at 40° for 16 hr. and at the reflux temperature for 1 hr. A portion of the brown solution was examined by g.l.c. (10% CAR, 180°; 3% APL, 160° and 220°) with bibenzyl as internal standard, and was found to contain biphenyl (31.7m/100m). Phenyl acetate (0.2m/100m would have been detected), acetanilide (1.0) and 1-phenylbenzotriazole

(0.5) were absent.

The bulk (23.0 mmoles nitrosamide) of the reaction mixture was chromatographed on alumina (420g.). Elution with petroleum-benzene (10:1) gave biphenyl (crude 1.23g., 7.96 mmoles, 34.6m/100m), m.p. and mixed m.p. 68-9° after crystallisation from methanol.

Elution with petroleum-benzene (5:1) afforded a colourless solid (0.155g.) which was crystallised from chloroform at -40° to yield p-terphenyl (0.016g., 0.07 mmole, 0.3m/100m; crude, 2.9m/100m), m.p. 212-3°, mixed m.p. 213-4°. The i.r. spectrum was indistinguishable from that of the authentic material.

N.m.r. (CDCl<sub>3</sub>):  $\tau$  2.25-2.79 (complex, with a singlet at 2.32).

No further appreciable fractions were obtained until the column was eluted with methanol, when brown tars resulted.

## 2. Reaction with Furan in Benzene

N-Nitrosoacetanilide (8.01g., 48.9 mmoles) was allowed to decompose in a solution of furan (6.8g., 0.10 mole) in benzene (46.8g., 0.60 mole). A sample of the reaction mixture was examined by g.l.c. (10% CAR, 180°; 10% SIL, 170°; 3% APL, 130°) with bibenzyl as internal standard, and was found to contain phenyl acetate (1.0m/100m), 2-phenylfuran (22.6) and biphenyl (16.9). 1,4-Dihydro-naphthalene-1,4-endoxide (0.15m/100m would have been

detected) was absent.

The yield of acetic acid (79.6m/100m) was determined by titration.

### 3. Reaction with 2,5-Dimethylfuran in Benzene

N-Nitrosoacetanilide (4.97g., 30.3 mmoles) was allowed to decompose in a solution of 2,5-dimethylfuran (5.76g., 60.0 mmoles) in benzene (28.1g., 0.36 mole). A sample of the brown solution was examined by g.l.c. (2% NPGS, 103°; 8% BDS, 160°) with bibenzyl as internal standard and was found to contain biphenyl (7.4m/100m) and an unidentified component (ca. 4.5 x weight of biphenyl) with a retention time on NPGS of 0.71 relative to biphenyl. Phenyl acetate (0.2m/100m would have been detected) and 1,4-dimethyl-1,4-dihydronaphthalene-1,4-endoxide (0.1) were absent.

Distillation of the bulk (25.8 mmoles nitrosamide) of the reaction mixture afforded a yellow oil (1.50g.), b.p. 82-4°/2.2 mm. Preparative g.l.c. (15 ft. x 0.375 in.o.d. glass column containing 20% APL on celite at 215°) afforded samples of biphenyl, m.p. and mixed m.p. 68-9°; and 2-benzyl-5-methylfuran, a pale yellow liquid, b.p. 130° (block temp.)/12 mm. (Found: C, 83.4; H, 7.0.  $C_{12}H_{12}O$  requires C, 83.7; H, 7.0%).

N.m.r. ( $CCl_4$ ):  $\tau$  2.87 (s, 5H, Ph), 4.29 (s, 2H,  $H_3$  and  $H_4$ ), 6.18 (s, 2H, methylene) and 7.79 (Me). All



four singlets appeared very slightly  
broadened when expanded.

I.r. (liquid): 1570, 1495, 1455, 1220, 1020, 780 and 715  $\text{cm}^{-1}$ .  
The yield of 2-benzyl-5-methylfuran (29.4m/100m) was  
computed from the quantitative g.l.c. measurements.

In a control experiment acetic acid (2.5 mmoles) was  
added to a solution of 1,4-dimethyl-1,4-dihydronaphthalene-  
1,4-endoxide (0.5 mmole) and biphenyl (0.5 mmole) in  
benzene (30 mmoles). G.l.c. examination (2% NPGS,  $103^{\circ}$ )  
showed that the ratio of endoxide to biphenyl was unchanged  
by the addition of acetic acid. The mixture was then boiled  
under reflux for 2.5 hr. after which time only a small  
reduction (2-5%) in the amount of endoxide was detected.

#### D Reactions of o-t-Butyl-N-nitrosoacetanilide

##### 1. Decomposition in Benzene

(a) The nitrosamide (0.986g., 4.48 mmoles) decomposed  
rapidly in benzene (7.02g., 0.090 mole) giving a dark  
red-brown solution, which was examined by g.l.c. (Table 1,  
p. 141) with fluorene as internal standard.

The yield of acetic acid (38m/100m) was determined by  
titration.

(b) o-t-Butyl-N-nitrosoacetanilide (2.59g., 11.8 mmoles)  
was allowed to decompose in benzene (17.6g., 0.236 mole).  
The bulk (11.0 mmoles nitrosamide) of the reaction

mixture was washed with 10% sodium hydrogen carbonate solution (13 ml.) and water, dried over magnesium sulphate, and filtered. Decalin (5.0g.) and *p*-xylene (0.45g.) were added to the filtrate which was then distilled through the spinning-band column to give five colourless liquid fractions: (i) 15.0g., b.p. 79-80.5°, (ii) 0.398g., b.p. 81-110°/123 mm., (iii) 0.387g., b.p. 110-120°/123 mm., (iv) 0.732g., b.p. 120-24°/123 mm., and (v) 0.603g., b.p. 124-26°/123 mm. Examination of the fractions by g.l.c. (20% APL, 210°) indicated that only (ii) and (iii) contained a major component with a retention time equal to that of *t*-butylbenzene. Preparative g.l.c. (20 ft. x 0.375 in.o.d. glass column containing 20% APL on celite, 159°) of these two fractions yielded *t*-butylbenzene (0.121g., 0.903 mmole, 8.2m/100m), identified by comparison of its i.r. and n.m.r. spectra with those of an authentic specimen. The material isolated in this way had a purity of at least 99.9% (g.l.c.).

## 2. Decomposition in Benzene-d<sub>6</sub>

*o*-*t*-Butyl-*N*-nitrosoacetanilide (1.90g., 8.62 mmoles) was allowed to decompose in benzene-d<sub>6</sub> (14.2g., 0.169 mole). The bulk (8.44 mmoles nitrosamide) of the reaction mixture was stirred with anhydrous sodium carbonate (0.53g.) for 8 hr., and filtered. Decalin (5 ml.) and *p*-xylene (0.3g.) were added to the filtrate which was fractionally distilled as in the previous experiment. Preparative g.l.c. of the



appropriate fractions yielded t-butylbenzene (0.118g.; assuming  $M = 134$ , 0.881 mmole, 10.4m/100m).

Mass spectrum: calculated from m/e 134, 135 etc.

$$C_{10}H_{14} = 95.4\%, C_{10}H_{13}D = 4.5\%,$$

$$C_{10}H_{12}D_2 = 0.1\%.$$

Calculated from m/e 119, 120 etc.

$$C_{10}H_{14} = 95.2\%, C_{10}H_{13}D = 4.8\%.$$

The i.r. and n.m.r. spectra were indistinguishable from those of authentic t-butylbenzene ( $C_{10}H_{14}$ ).

### 3. Reaction with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene

o-t-Butyl-N-nitrosoacetanilide (5.47g., 24.9 mmoles) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (12.7g., 32.9 mmoles) in benzene (39.0g., 0.500 mole). The cooled reaction mixture was filtered, the solid material washed with benzene, and samples of the combined filtrate and washings examined by g.l.c. (Table 1, p. 141) with fluorene as internal standard.

The yield of acetic acid (52.5m/100m) was determined by titration.

The major part (21.6 mmoles nitrosamide) of the filtrate and all the solid matter collected by filtration were combined and chromatographed on alumina (1000g.). Elution

with petroleum-benzene (5:1) gave an oily solid (0.168g.) which, from ethanol at  $-40^{\circ}$ , afforded colourless crystals of 2-*t*-butylbiphenyl (0.080g., 0.38 mmole, 1.8m/100m; crude, 3.7m/100m), m.p. and mixed m.p.  $36-7^{\circ}$ . The i.r. spectrum was identical to that of the authentic biaryl.

Elution with petroleum-benzene (1:1) gave a brown solid (3.61g.) which was crystallised from petroleum and from acetic acid to yield colourless 5-*t*-butyl-1,2,3,4-tetraphenyl-naphthalene (3.005g., 6.25 mmoles, 28.9m/100m; crude, 34.2m/100m), m.p.  $162-3^{\circ}$ . (Found: C, 93.4; H, 6.6.  $C_{38}H_{32}$  requires C, 93.4; H, 6.6%).

N.m.r. spectrum: see Appendix.

$\lambda_{\text{max.}}$  (log  $\epsilon$ ) in petroleum: 247(4.59), 252(4.61), 254.5(4.59), 276sh(4.23) and 320  $m\mu$ (4.05).

2,3,4,5-Tetraphenylcyclopentadienone (7.77g., 20.2 mmoles) was eluted in benzene.

#### 4. Reaction with Furan in Benzene

o-*t*-Butyl-N-nitrosoacetanilide (6.39g., 29.05 mmoles) was allowed to decompose in a solution of furan (3.95g., 58.0 mmoles) in benzene (45.3g., 0.580 mole), and a sample of the orange reaction mixture was examined by g.l.c. (Table 1, p. 141) with fluorene as internal standard.

The yield of acetic acid (56.5m/100m) was determined by titration.

The bulk (24.15 mmoles nitrosamide) of the reaction mixture was distilled to give: (i) a liquid, b.p. 32-82°, (ii) a liquid (0.037g.), b.p. 25-40°/21 mm., (iii) a liquid (0.436g.), b.p. 46-52°/0.05 mm., (iv) a pale green liquid (1.140g.), b.p. 49-54°/0.04 mm., (v) a pale green liquid (1.475g.), b.p. 54-58°/0.04 mm., (vi) a pale green liquid (0.248g.), b.p. 58-9°/0.04 mm., (vii) a red oil (0.532g.), b.p. 59-110°/0.04 mm., and (viii) a brown residue (0.699g.). After examination of all the fractions by g.l.c. (2% NPGS, 140°), fractions (v)-(vii) were combined and crystallised from petroleum at -60° to yield 5-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (0.657g., 3.285 mmoles, 13.7m/100m), m.p. 56-7°. (Found: C, 83.8; H, 8.5.  $C_{14}H_{16}O$  requires C, 84.0; H, 8.1%). N.m.r. spectrum: see Appendix. I.r. (melt): 1395 and 1365 (t-Bu); 1125 (C-O-C); and 715  $cm^{-1}$  (cis CH=CH).

The crystallisation mother-liquors were combined with fraction (iv) and redistilled to give four colourless liquid fractions: (ix) 0.074g., b.p. to 123°/18 mm., (x) 0.626g., b.p. 123-6°/18 mm., (xi) 0.669g., b.p. 126°/18mm., and (xii) 0.597g., b.p. 126-38°/18 mm. Fraction (xi) was identified as o-*t*-butylphenyl acetate by comparison of its refractive index and i.r. spectrum with those of the authentic ester. G.l.c. examination (2% NPGS, 140°)

140.

indicated that fractions (x)-(xii) consisted of ca. 90% of the acetate (ca. 1.70g., 8.86 mmols, 36.8m/100m).

TABLE 1Reactions of o-t-Butyl-N-nitrosoacetanilide

Product	Yield (m/100m of nitrosamide) by g.l.c.		
	Reaction D.1(a)	D.3	D.4
t-Butylbenzene	10.2	3.2	3.5
<u>o</u> -t-Butylphenyl acetate	37.8	50.5	36.9
<u>m</u> -t-Butylphenyl acetate	17.4	<1.0	<0.8
Biphenyl	3.9	0.2	0.9
2-t-Butylbiphenyl	2.3	2.6	3.0
<u>o</u> -t-Butylacetanilide	0.3	0.7	1.9
5-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide	-	-	20.5

3- and 4-t-Butylbiphenyls (0.5m/100m would have been detected), p-t-butylphenyl acetate (1.0) and o-, m-, and p-t-butylphenols (0.7) were absent.

Quantitative measurements were made on 2% CAR, 148°; and for t-butylbenzene on 10% PEGA, 156°. The identities of products were confirmed on 3% APL, 175°. o-, m-, and p-t-Butylphenyl acetate each gave the same response to a flame-ionisation detector; their ratio was determined on 2% NPGS, 100° and confirmed on CAR capillary, 160°.

## E Reactions of p-t-Butyl-N-nitrosoacetanilide

### 1. Decomposition in Benzene

The nitrosamide (5.59g., 25.4 mmoles) decomposed rapidly in benzene (39.0g., 0.500 mole). A sample of the reaction mixture was examined by g.l.c. (Table 2, p. 151) with bibenzyl as internal standard.

The yield of acetic acid (85.5m/100m) was determined by titration.

The major part (21.95 mmoles nitrosamide) of the reaction mixture was distilled to give: (i) a colourless liquid b.p. 79-81°, (ii) a yellow oil which solidified (2.00g.), b.p. 114-6°/0.05 mm., (iii) an orange sublimate (0.720g.), bath temp. to 200°/0.05 mm., and (iv) a black residue (1.23g.). Fraction (ii), crystallised from ethanol at -20°, yielded colourless 4-t-butylbiphenyl (1.50g., 7.14 mmoles, 32.6m/100m), m.p. 51.5-52° (lit.,<sup>153</sup> 52.2°). N.m.r. (CCl<sub>4</sub>):  $\tau$  2.34-2.86 (complex, 9H) and 8.67 (t-Bu).

Crystallised from ether, fraction (iii) afforded p-t-butyl-acetanilide (0.140g., 0.73 mmole, 3.3m/100m), m.p. and mixed m.p. 172-3°. The i.r. spectrum was identical to that of the authentic amide.

### 2. Decomposition in Benzene-d<sub>6</sub>

p-t-Butyl-N-nitrosoacetanilide (2.69g., 12.2 mmoles) was allowed to decompose in benzene-d<sub>6</sub> (20.0g., 0.238 mole), and a

portion (11.9 mmoles nitrosamide) of the reaction mixture was worked-up as in experiment D.2 to give *t*-butylbenzene (0.0771g.; assuming  $M = 134$ , 0.575 mmole, 4.8m/100m).

Mass spectrum: calculated from  $m/e$  134, 135 etc.

$$C_{10}H_{14} = 69.0\%, C_{10}H_{13}D = 30.7\%,$$

$$C_{10}H_{12}D_2 = 0.3\%.$$

Calculated from  $m/e$  119, 120, etc.

$$C_{10}H_{14} = 68.2\%, C_{10}H_{13}D = 31.8\%.$$

N.m.r. ( $CCl_4$ ): some simplification of absorption at  $\tau$  2.55-3.05 relative to  $C_{10}H_{14}$ .

I.r. (liquid): bands at 2270, 2250 (very weak), 1410 (weak) and  $850\text{ cm.}^{-1}$  (medium) not present in spectrum of  $C_{10}H_{14}$ .

### 3. Reaction with 2,3,4,5-Tetraphenylcyclopentadienone in

#### Benzene

(a) *p*-*t*-Butyl-*N*-nitrosoacetanilide (5.79g., 26.3 mmoles) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (12.7g., 33.0 mmoles) in benzene (39.0g., 0.500 mole). The cooled reaction mixture was filtered, the solid material washed with benzene, and a sample of the combined filtrate and washings was examined by g.l.c. (Table 2, p.151) with bibenzyl as internal standard.

The yield of acetic acid (75.5m/100m) was determined by titration.



Distillation of the bulk (22.8 mmoles nitrosamide) of the filtered reaction mixture gave a sample of *p*-*t*-butylphenyl acetate (0.030g., 0.156 mmole, 0.7m/100m), bath temp. to 200°/16 mm., identical (refractive index and i.r. spectrum) with the authentic ester.

(b) The product from a similar reaction of the nitrosamide (5.84g., 26.5 mmoles) with 2,3,4,5-tetraphenylcyclopentadienone (12.7g., 33.0 mmoles) in benzene was chromatographed on alumina (1000g.). Elution with petroleum-benzene (9:1) gave a colourless solid (0.272g.) which was crystallised from ethanol at -20° to yield 4-*t*-butylbiphenyl (0.166g., 0.791 mmole, 3.0m/100m; crude, 4.9m/100m), m.p. 50-51°; mixed with the biaryl from E.1, m.p. 50-51°. The i.r. spectrum was identical to that of 4-*t*-butylbiphenyl from E.1.

Elution with petroleum-benzene (3:2) gave an oily brown solid which was washed with very little cold petroleum to afford a white powder (1.56g.). By crystallisation from benzene-methanol (5:2) there was obtained 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene (1.38g., 2.83 mmoles, 10.7m/100m; crude, 12.1m/100m), m.p. 285.5-6.5°. (Found: C, 93.35; H, 6.7.  $C_{38}H_{32}$  requires C, 93.4; H, 6.6%). The m.p. was not depressed by admixture of this product with 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene prepared from an authentic aryne source (see Section VI).

N.m.r. spectrum: see Appendix.

$\lambda_{\text{max.}}$  (log  $\epsilon$ ) in petroleum: 241 (4.67), 246(4.69), 250(4.67)  
255(4.59), 260sh(4.48), and  
296 m $\mu$ (4.09).

I.r. (Nujol): 1070, 830, 750, 740 and 700 cm.<sup>-1</sup> Weak bands  
included 662 and 643 cm.<sup>-1</sup>

2,3,4,5-Tetraphenylcyclopentadienone (10.3g., 26.9 mmoles)  
was eluted in benzene.

#### 4. Reaction with Furan in Benzene

p-t-Butyl-N-nitrosoacetanilide (6.16g., 28.0 mmoles) was  
allowed to decompose in a solution of furan (3.81g., 56.0 mmoles)  
in benzene (43.6g., 0.560 mole). Samples of the orange reaction  
mixture were examined by g.l.c. (Table 2, p.151) with biphenyl  
and bromobenzene as internal standards. The major part  
(18.0 mmoles nitrosamide) of the reaction mixture was distilled  
to give: (i) a colourless liquid, b.p. 65-86°, (ii) a  
colourless liquid (0.020g.), bath temp. to 100°/0.04 mm., and  
(iii) a yellow oil (1.27g.), b.p. 66-88°/0.04 mm. Fraction  
(iii) was seen by g.l.c. examination (2% NPGS, 135°) to  
contain two principal components. Preparative g.l.c.  
(7 ft. x 0.375 in.o.d. glass column containing 10% NPGS  
on celite, 200°) allowed isolation of samples of 4-t-butyl-  
biphenyl, m.p. and mixed m.p. 50-51°; and 2-(p-t-butylphenyl)-  
furan b.p. 56°/0.04 mm. (Found: C, 83.5; H, 8.4. C<sub>14</sub>H<sub>16</sub>O

requires C, 84.0; H, 8.05%).

N.m.r. ( $\text{CCl}_4$ ):  $\tau$  2.54 (centre of  $\text{AA}'\text{BB}'$ ,  $1\text{H}$ ), 2.58 (dd,  $\text{H}_5$ ),  
3.45 (dd,  $\text{H}_3$ ), 3.61 (dd,  $\text{H}_4$ ) and 8.69 (t-Bu).

$J_{3-4}$  3.5,  $J_{3-5}$  0.8 and  $J_{4-5}$  1.6 c./sec.

I.r. (liquid): 1395 and 1365 (t-Bu); 1020, 1010, 800 and  
730  $\text{cm}^{-1}$

##### 5. Reaction with "Galvinoxyl" in Benzene

p-t-Butyl-N-nitrosoacetanilide was allowed to decompose in benzene (20m/mole of nitrosamide) containing "Galvinoxyl" (0.188 and 0.045 m/mole of nitrosamide). A control experiment, using part of the same sample of nitrosamide, was run under identical conditions, but in the absence of "Galvinoxyl". Portions of the reaction mixtures were analysed by g.l.c. (2% NPGS,  $179^\circ$ ; 10% SIL,  $81^\circ$ ) with phenanthrene and cumene as internal standards.

##### Reagents (mmoles)

<u>p</u> -t-Butyl-N-nitrosoacetanilide	5.19	5.21	5.14
"Galvinoxyl"	0.977	0.236	0.000

##### Products (m/100m of nitrosamide)

t-Butylbenzene	1.4	3.1	4.6
<u>p</u> -t-Butylphenyl acetate	1.3	1.6	1.0
4-t-Butylbiphenyl	13.1	26.3	30.4
<u>p</u> -t-Butylacetanilide	10.1	9.7	10.7

6. Re-examination of the Reaction of p-t-Butyl-N-nitroso-acetanilide with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene.

Authentic specimens of 6-t-butyl-1,2,3,4-tetraphenylnaphthalene (XIX) and 1-(p-t-butylphenyl)-2,3,4-triphenylnaphthalene (XX) having been prepared, the decomposition of p-t-butyl-N-nitroso-acetanilide (3.49g., 15.85 mmoles) in benzene (23.4g., 0.300 mole), in the presence of 2,3,4,5-tetraphenylcyclopentadienone (7.15g., 18.6 mmoles) was re-examined. A portion (7.93 mmoles nitrosamide) of the reaction mixture was chromatographed on alumina (500g.). Elution with petroleum containing an increasing proportion of benzene (0-60%) allowed 19 x 300 ml. fractions to be collected before 2,3,4,5-tetraphenylcyclopentadienone began to be eluted. The authentic isomeric adducts were not resolved by t.l.c. on alumina with petroleum-benzene (3:2), both having  $R_f$  0.80. The chromatography fractions were examined by t.l.c., and those (13-17, total 0.489g.) with a component  $R_f$  0.80 were combined. The i.r. spectra of the following solutions in carbon tetrachloride were obtained using 3 mm. silver chloride cells:

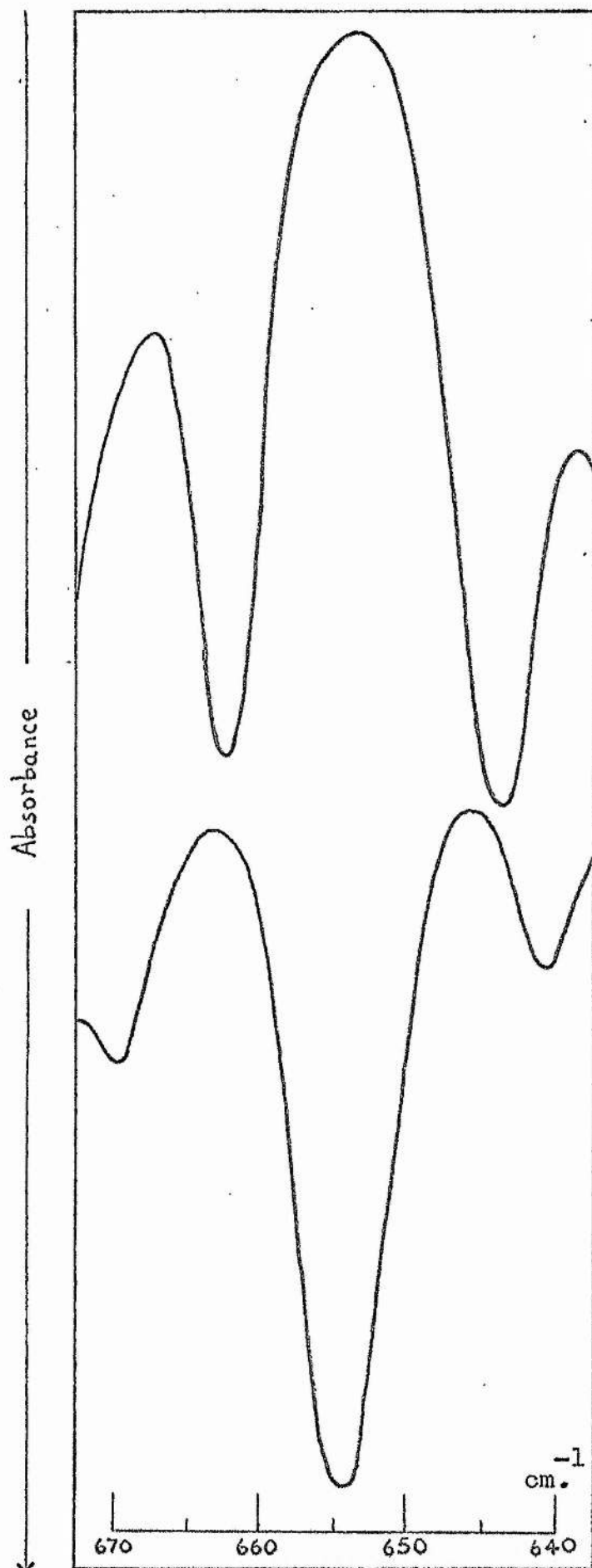
1. Adduct (XIX), 24.45 g.l.<sup>-1</sup>
2. Adduct (XX), 22.1 g.l.<sup>-1</sup>
3. Adduct (XIX) + adduct (XX), 20.4 + 3.68 g.l.<sup>-1</sup>

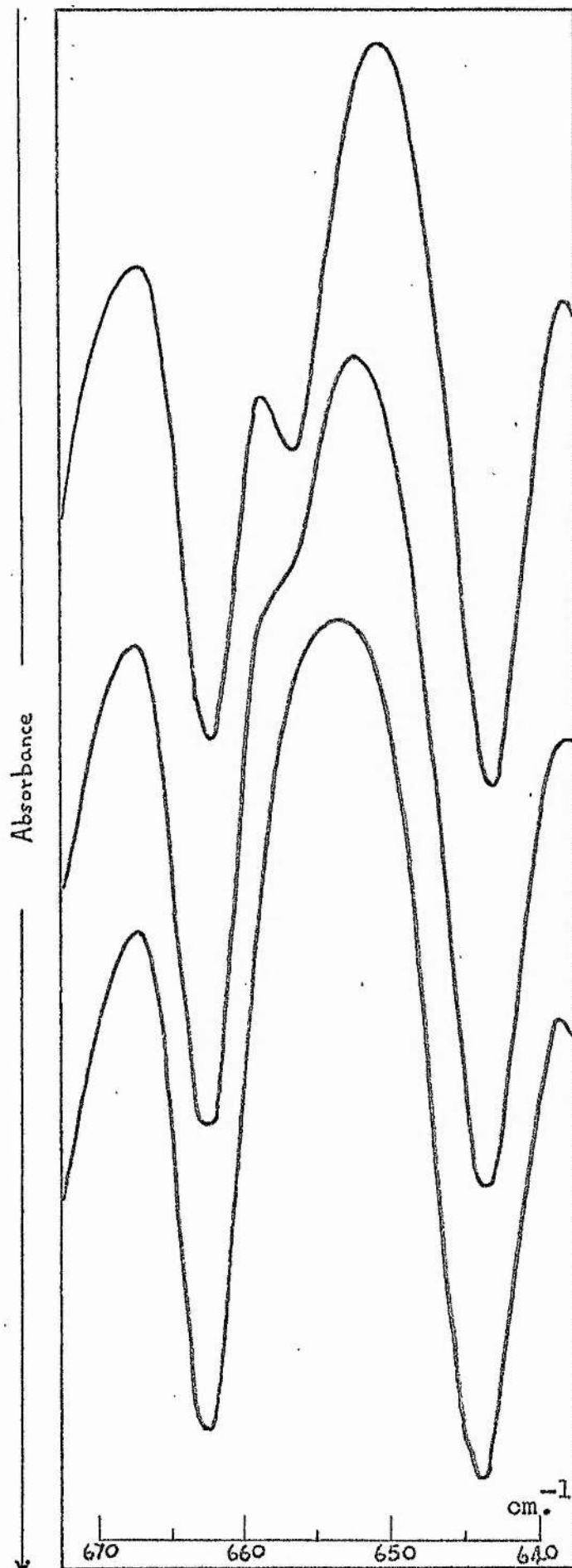
4. Adduct (XIX) + adduct (XX), 23.3 + 1.05 g.l.<sup>-1</sup>

5. Chromatography fractions 13-17, 24.45 g.l.<sup>-1</sup>

A part of each of these spectra (670-640 cm.<sup>-1</sup>) is reproduced on the following pages. Spectrum 5 of the reaction product was identical to spectrum 1 of adduct (XIX), and could be distinguished from spectra 2-4 by the absence of a band at ca. 655 cm.<sup>-1</sup> The crude adduct (1.00 mmole, 12.6m/100m) therefore consisted of less than 4.3% (0.55m/100m nitrosamide) of 1-(p-t-butylphenyl)-2,3,4-triphenylnaphthalene.

The n.m.r. spectra of (XIX) and (XX) differed in- sufficiently to allow discrimination between the spectrum of pure (XIX) and that of a mixture of (XIX) and (XX) (15:1). No shift of the resonance frequency of the t-butyl group in either adduct was observed when the spectra were obtained in deuteriochloroform containing benzene.

I.R. SPECTRASpectrum 1 - Adduct (XIX)Spectrum 2 - Adduct (XX)

I.R. SPECTRASpectrum 3

Adduct (XIX) + adduct (XX)

Spectrum 4

Adduct (XIX) + adduct (XX)

Spectrum 5

Reaction product



TABLE 2Reactions of p-t-Butyl-N-nitrosoacetanilide

Product	Yield (m/100m of nitrosamide) by g.l.c.		
	Reaction E.1	E.3(a)	E.4
t-Butylbenzene	5.9	0.3	5.8
p-t-Butylphenyl acetate	0.5	8.7	0.3
Biphenyl	0.4	< 0.2	0.1
4-t-Butylbiphenyl	36.4	4.8	18.6
p-t-Butylacetanilide	5.8	5.7	8.7
2-(p-t-Butylphenyl)furan	-	-	16.6

o- and m-t-Butylphenyl acetates (0.2m/100m would have been detected), 2- and 3-t-butylbiphenyls (0.2) and o-, m-, and p-t-butylphenols (0.2) were absent from all reactions; 6-t-butyl-1,4-dihydronaphthalene-1,4-endoxide (0.2), 2-phenyl-furan (0.1) and 2-(m-t-butylphenyl)furan (0.1) were absent from reaction E.4.

Quantitative measurements were made on 10% CAR, 155° and 2% NPGS, 168° [reactions E.1 and E.3 (a)]; or on 10% CAR, 168° and 2% CAR, 156° (reaction E.4); except t-butylbenzene which was estimated on 10% SIL, 120° [reactions E.1 and E.3 (a)] or 10% CAR, 99° (reaction E.4, with bromobenzene as internal standard).

## F Reactions of *m*-*t*-Butyl-*N*-nitrosoacetanilide

### 1. Decomposition in Benzene

*m*-*t*-Butylacetanilide (5.73g., 30.0 mmoles) was nitrosated and the reaction mixture poured into iced water (200 ml.). The yellow oil which separated was extracted with cold benzene (25, 10, 5 ml.) and the combined extracts were washed with iced water (2 x 25 ml.), 5% potassium hydrogen carbonate solution (2 x 25 ml.), and water (2 x 25 ml.). The benzene solution was stirred with magnesium sulphate for 1 hr. and with phosphorus pentoxide for 5 min., the temperature being kept below 5°. Solid matter was removed by filtration and washed with benzene, and the filtrate and washings were combined to give a solution of *m*-*t*-butyl-*N*-nitrosoacetanilide (assumed 30.0 mmoles) in benzene (46.8g., 0.60 mole), which was allowed to react. A sample of the reaction mixture was examined by g.l.c. (Table 3, p. 157) with phenanthrene as internal standard.

The bulk (27.0 mmoles nitrosamide) of the reaction mixture gave on distillation: (i) a liquid, b.p. 79-121°, (ii) a liquid (0.227g.), b.p. to 32°/0.05mm., (iii) a colourless oil (0.180g.), b.p. 32-70°/0.1 mm., (iv) a yellow oil (2.29g.), b.p. 78-92°/0.05 mm., and (v) a residue (2.20g.). Fraction (iii) was crystallised from petroleum at -60° to yield *m*-*t*-butylphenyl acetate (0.08g., 0.468

mmole, 1.7m/100m), n.p. and mixed m.p. 41-2°. The i.r. spectrum was identical to that of the authentic specimen.

Fraction (iv) was chromatographed on alumina (150g.). Elution with petroleum yielded 3-t-butylbiphenyl (1.11g., 5.29 mmole, 19.6m/100m), b.p. 74°/0.05 mm. (lit., <sup>153</sup>105°/0.4 mm.).

N.m.r. (CCl<sub>4</sub>):  $\tau$  2.35-2.85 (complex, 9H) and 8.64 (t-Bu). A small absorption at 8.48 (s, ca. 0.5H) was attributed to an unidentified impurity. I.r. (liquid): 1390 and 1365 cm.<sup>-1</sup> (t-Bu).

## 2. Reaction with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene

A dry solution of m-t-butyl-N-nitrosoacetanilide (30.0 mmole) in benzene (46.8g., 0.60 mole) was prepared as above and 2,3,4,5-tetraphenylcyclopentadienone (15.4g., 40.0 mmole) added. The nitrosamide was allowed to decompose, the reaction mixture filtered, and the solid material washed with benzene. A portion of the combined filtrate and washings was examined by g.l.c. (Table 3, p. 157) with phenanthrene as internal standard.

The major part (27.3 mmole nitrosamide) of the filtrate, together with all the solid matter, was chromatographed on alumina (Brockmann activity = 1). Elution with petroleum-benzene (3:1) gave 3-t-butylbiphenyl (0.190g., 0.905 mmole,

3.3m/100m), having an i.r. spectrum indistinguishable from that of the biaryl from the previous experiment.

Elution with petroleum-benzene (4:5) gave a pale brown oily solid (1.61g.) which was stirred with boiling petroleum (15 ml.). From the cooled suspension 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene (0.836g., 1.72 mmoles, 6.3m/100m), m.p. 286-7°, was filtered off. The m.p. was unchanged when this product was mixed with the adduct formed from *p*-*t*-butyl-*N*-nitrosoacetanilide; the i.r. spectra were identical.

Concentration of the petroleum mother-liquor (to 8 ml.), followed by refrigeration, afforded 5-*t*-butyl-1,2,3,4-tetraphenylnaphthalene (0.520g., 1.07 mmoles, 3.9m/100m), m.p. 164.5-5.5°; mixed with the adduct formed from *o*-*t*-butyl-*N*-nitrosoacetanilide, (D.3), m.p. 161-2°. The i.r. and n.m.r. spectra were identical to those of the adduct from D.3, and clearly different from the i.r. and n.m.r. spectra of 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene.

The total yield of the two adducts (crude, 1.61g.) was 12.1m/100m.

2,3,4,5-Tetraphenylcyclopentadienone (12.3g., 32.2 mmoles) was eluted in benzene.

### 3. Reaction with Furan in Benzene

Furan (4.08g., 60.0 mmoles) was added to a dry solution of *m*-*t*-butyl-*N*-nitrosoacetanilide (30.0 mmoles) in benzene

(62g., 0.79 mole) prepared as in F.1. The nitrosamide was allowed to decompose and portions of the reaction mixture were examined by g.l.c. (Table 3, p.157) with biphenyl and o-bromotoluene as internal standards. Under the conditions employed, 3-t-butylbiphenyl and (authentic) 6-t-butyl-1,4-dihydronaphthalene-1,4-endoxide were only partially resolved. The separation on 10% PEGA, 140° was sufficient to allow detection of both components in a mixture of the biaryl and the endoxide (25:1 by weight). No endoxide was detected in the reaction mixture. T.l.c. on alumina confirmed the absence (0.6m/100m would have been detected) of 6-t-butyl-1,4-dihydronaphthalene-1,4-endoxide.

Distillation of the bulk (24.9 mmoles nitrosamide) of the reaction mixture gave: (i) a liquid, b.p. 60-86°, (ii) a liquid (3.12g.), b.p. 38-57°/36 mm., (iii) a liquid (0.582 g.), b.p. to 48°/15 mm., (iv) a yellow oil (1.844g.), b.p. 58-76°/0.04 mm., and (v) a viscous yellow oil (1.37g.), b.p. 76-84°/0.04 mm. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% NPGS on celite at 190°) of fraction (iv) yielded three products:

3-t-butylbiphenyl, identified by comparison of its i.r. spectrum with that of the biaryl from F.1;

m-t-butylphenyl acetate, identified by its m.p., mixed m.p., and i.r. spectrum; and

2-(m-t-butylphenyl)furan, a colourless liquid after distillation, b.p.  $90^{\circ}$  (block temp.)/0.8 mm. (Found: C, 83.3; H, 8.06.  $C_{14}H_{16}O$  requires C, 84.0; H, 8.05%).

N.m.r. ( $CCl_4$ ):  $\tau$  2.27-2.85 (complex, 4H), 2.59 (dd,  $H_5$ ), 3.43 (dd,  $H_3$ ), 3.61 (dd,  $H_4$ ) and 8.64 (t-Bu).  
 $J_{3-4}$  3.3,  $J_{3-5}$  0.9 and  $J_{4-5}$  1.8 c./sec.

I.r. (liquid): 1390 and 1365 (t-Bu), 1015, 790, 775, 735, 700 and 685  $cm^{-1}$ .

Mass spectrum: Parent ion, m/e 200.  $C_{14}H_{16}O$  requires  $M = 200$ .  
 $M + 1/M = 16.18\%$ .  $C_{14}H_{16}O$  requires  $M + 1/M = 15.42\%$ .  
 $M + 2/M = 1.64\%$ .  $C_{14}H_{16}O$  requires  $M + 2/M = 1.31\%$ .  
 Metastable peaks at 171.2, 150.9, 133.1 and 105.7.

TABLE 3Reactions of m-t-Butyl-N-nitrosoacetanilide

Product	Yield (m/100m of nitrosamide) by g.l.c.		
	Reaction F.1	F.2	F.3
t-Butylbenzene	4.2	0.5	8.7
<u>m</u> -t-Butylphenyl acetate	7.9	17.2	9.0
Biphenyl	0.3	0.1	0.3
3-t-Butylbiphenyl	19.4	4.6	11.2
<u>m</u> -t-Butylacetanilide	14.2	17.1	13.1
2-( <u>m</u> -t-butyl)phenylfuran	-	-	7.0

o- and p-t-Butylphenyl acetates (0.2m/100m would have been detected), 2- and 4-t-butylbiphenyls(0.3) and o-, m-, and p-t-butylphenols (0.4) were absent from all reactions; 5- and 6-t-butyl-1,4-dihydronaphthalene-1,4-endoxides (0.4 and 0.6), 2-phenylfuran (0.7) and 2-(p-t-butylphenyl)furan (0.1) were absent from reaction F.3.

Quantitative measurements were made on 2% CAR, 148° (reactions F.1 and F.2) or 10% CAR, 168° and 2% CAR, 156° (reaction F.3), except that t-butylbenzene was estimated on 10% SIL, 120° (reactions F.1 and F.2) or 10% AFL, 106° (reaction F.3, with o-bromotoluene as internal standard).



G Reactions of o- and p-t-Butyl-N-nitroso-2,2,2-trideuterioacetanilides

1. Decomposition in Benzene

(a) o-t-Butyl-N-nitroso-2,2,2-trideuterioacetanilide (4.33g., 19.4 mmoles) was allowed to decompose in benzene (30.2g., 0.388 mole), and the bulk (16.35 mmoles nitrosamide) of the reaction mixture was worked up as in experiment D.1 to give t-butylbenzene (0.207g., assuming  $M = 134$ , 1.55 mmoles, 9.5m/100m).

Mass spectrum: calculated from  $m/e$  134, 135 etc.,

$$C_{10}H_{14} = 92.6\%, C_{10}H_{13}D = 7.3\%, C_{10}H_{12}D_2 = 0.1\%.$$

Calculated from  $m/e$  119, 120 etc.,

$$C_{10}H_{14} = 92.8\%, C_{10}H_{13}D = 7.2\%.$$

The i.r. and n.m.r. spectra were identical to those of  $C_{10}H_{14}$ .

(b) p-t-Butyl-N-nitroso-2,2,2-trideuterioacetanilide (4.11g., 18.45 mmoles) was allowed to decompose in benzene (28.8g., 0.369 mole), and the bulk (17.5 mmoles nitrosamide) of the reaction mixture was worked up as in experiment D.1 to give t-butylbenzene (0.108g.; assuming  $M = 134$ , 0.809 mmoles, 4.6m/100m).

Mass spectrum: calculated from  $m/e$  134, 135 etc.,

$$C_{10}H_{14} = 97.9\%, C_{10}H_{13}D = 2.1\%, C_{10}H_{12}D_2 = 0.0\%.$$

Calculated from  $m/e$  119, 120 etc.,

$$C_{10}H_{14} = 97.4\%, C_{10}H_{13}D = 2.6\%.$$

The i.r. and n.m.r. spectra were identical to those of  $C_{10}H_{14}$ .

## H Reactions of 2,5-Di-*t*-butyl-*N*-nitrosoacetanilide

### 1. Decomposition in Benzene

The nitrosamide (5.00g., 18.1 mmoles) decomposed slowly in benzene (70.2g., 0.90l mole) to give a dark red solution, a sample of which was examined by g.l.c. (Table 4, p. 164) with fluorene as internal standard.

The bulk (14.9 mmoles nitrosamide) of the reaction mixture afforded on distillation: (i) a colourless liquid, b.p. 78°, (ii) a white sublimate (0.100g.), bath temp. to 100°/0.4 mm., (iii) a yellow oil which solidified (3.16g.), b.p. 66-70°/0.05 mm., and (iv) a brown residue (0.537g.). Fraction (ii) was *p*-di-*t*-butylbenzene (crude, 0.52 mmole, 3.5m/100m), m.p. and mixed m.p. 75-6° after crystallisation from methanol.

Fraction (iii), seen by g.l.c. examination (10% SIL, 180°) to contain one major component, was crystallised from petroleum to yield colourless 2,5-di-*t*-butylphenyl acetate (1.05g., 4.23 mmoles, 28.5m/100m; crude, 85m/100m), m.p. 52-3°, mixed m.p. 51-2°. (Found: C, 77.4; H, 9.7. Calc. for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>: C, 77.4; H, 9.7%).

### 2. Reaction with 2,3,4,5-Tetraphenylcyclopentadienone in Benzene

2,5-Di-*t*-butyl-*N*-nitrosoacetanilide (5.62g., 20.4 mmoles) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (23.5g., 61.2 mmoles) in benzene (79.6g., 1.02 moles). The cooled reaction mixture was filtered, the

solid material washed with benzene, and a sample of the combined filtrate and washings was examined by g.l.c. (Table 4, p. 164) with fluorene as internal standard.

The major part (18.8 mmoles nitrosamide) of the filtrate was distilled to give: (i) a colourless liquid, b.p.  $78^{\circ}$ , (ii) a white sublimate (0.110g.), bath temp. to  $80^{\circ}/0.05$  mm., (iii) a yellow oil (3.36g.), b.p.  $66-70^{\circ}/0.05$  mm., and (iv) a residue (3.67g.). Fraction (ii) was p-di-t-butylbenzene (crude, 0.58 mmole, 3.4m/100m), m.p. and mixed m.p.  $76-7^{\circ}$  after crystallisation from methanol.

Fraction (iii) was 2,5-di-t-butylphenyl acetate (crude, 13.6 mmoles, 72.3m/100m), m.p. and mixed m.p.  $52-3^{\circ}$  after crystallisation from light-petroleum (b.p.  $60-80^{\circ}$ ).

The distillation residue (iv) was combined with all the solid collected by filtration and chromatographed on alumina (500g.). Elution with petroleum containing an increasing proportion of benzene (0-30%) gave 26 x 70 ml. fractions before 2,3,4,5-tetraphenylcyclopentadienone began to be collected. Fractions 17-21 gave a single diffuse spot on a silica t.l.c. plate developed with petroleum-benzene (1:1). They were combined to give an oily red solid (0.241g.) which was repeatedly crystallised from methanol and from isopropanol, but the product obtained was not sharp-melting and did not sublime at  $170^{\circ}$  (block temp.)/0.05 mm. The i.r. spectrum

showed an absorption at  $3510\text{ cm.}^{-1}$  (O-H). This material was not identified.

The remaining chromatography fractions contained only trace amounts of oils.

### 3. Reaction with Anthracene in Benzene

2,5-Di-*t*-butyl-*N*-nitrosoacetanilide (6.30g., 22.8 mmoles) was allowed to decompose in benzene (60.5g., 0.775 mole) containing anthracene (10.4g., 58.4 mmoles) in suspension. When the decomposition was complete, unreacted anthracene (8.49g., 47.6 mmoles) was filtered off and washed with benzene. The filtrate and washings were combined, and a sample was examined by g.l.c. (Table 4, p.164) with trans-stilbene as internal standard.

Volatile matter was distilled out from the bulk (22.3 mmoles nitrosamide) of the filtered reaction mixture, bath temp. to  $130^{\circ}/0.1\text{ mm.}$ , and *p*-di-*t*-butylbenzene (crude, 0.037g., 0.195 mmole,  $0.9\text{m}/100\text{m}$ ), m.p.  $73-4^{\circ}$ , and 2,5-di-*t*-butylphenyl acetate (crude, 2.99g., 12.05 mmoles,  $54.0\text{m}/100\text{m}$ ), m.p.  $50-51^{\circ}$  were isolated. The brown residue (3.59g.) was dissolved in xylene (22 ml.), maleic anhydride (2.05g.) added, and the mixture boiled under reflux for 25 min. After standing at room temperature for 3.5 hr., 2*N*-sodium hydroxide solution (40 ml.) was added and the mixture boiled under reflux for a further 2.25 hr. When cool, the organic layer

was separated, diluted with ether (100 ml.), washed with water (3 x 50 ml.), and dried over magnesium sulphate. The residue remaining after evaporation of the solvents under reduced pressure was chromatographed on alumina (300g.). Elution with petroleum-benzene (9:1) produced a blue-fluorescent solution which was evaporated to a pale orange solid (1.28g.). Crystallisation from light-petroleum (b.p. 60-80°) afforded colourless 1,4-di-*t*-butyltritycene (0.793g., 2.16 mmoles, 9.7m/100m; crude, 15.8m/100m), m.p. 233-4°.

(Found: C, 91.7; H, 8.25.  $C_{28}H_{30}$  requires C, 91.75; H, 8.25%).

N.m.r. ( $CCl_4$ ):  $\tau$  2.85 (centre of AA'BB', 8H), 3.10 (s, 2H,  $H_2$  and  $H_3$ ), 3.80 (s, 2H, bridge-head) and 8.43 (s, 18H, *t*-Bu).

$\lambda_{max.}$  (log  $\epsilon$ ) in methanol: 262.5 (3.17), 271 (3.36) and 279  $m\mu$  (3.46).

I.r. (Nujol): 1170, 825, 765, 745, 700 and 645  $cm^{-1}$ .

G.l.c. examination (3% APL, 250°) indicated that the anthracene filtered off from the reaction mixture contained no 1,4-di-*t*-butyltritycene, nor other contaminant. The quantity of anthracene in the filtrate (3.88 mmoles) was determined by g.l.c. (10% SIL, 189°) with trans-stilbene as internal standard, allowing the amount consumed in the reaction (30.3m/100m) to be computed.

#### 4. Decomposition in Furan

2,5-Di-*t*-butyl-N-nitrosoacetanilide (6.48g., 23.5 mmoles)

was allowed to decompose in furan (47.9g., 0.705 mole), giving a deep orange solution. A sample of the reaction mixture was examined by g.l.c. (Table 4, p. 164) with phenanthrene as internal standard.

The bulk (22.2 mmoles nitrosamide) of the reaction mixture was distilled to give: (i) a colourless liquid, b.p.  $32^{\circ}$ , (ii) a white sublimate (0.032g.), bath temp. to  $70^{\circ}/0.04$  mm., (iii) a yellow sublimate (0.035g.), bath temp. to  $80^{\circ}/0.04$  mm., (iv) a yellow oil which solidified (3.00g.), b.p.  $74-82^{\circ}/0.02$  mm., (v) a yellow oil (1.05g.), b.p.  $82^{\circ}/0.02$  mm., (vi) a yellow solid (0.765g.), bath temp. to  $165^{\circ}/0.02$  mm., and (vii) a black residue (0.609g.). The fractions were examined by g.l.c. (10% SIL,  $194^{\circ}$ ). Fractions (ii) and (iii) were largely *p*-di-*t*-butylbenzene (crude, 0.353 mmole, 1.6m/100m), which was isolated by crystallisation from methanol, m.p.  $75-6^{\circ}$ , mixed m.p.  $76-7^{\circ}$ .

Fractions (iv)-(vi) contained two principal components; 2,5-di-*t*-butylphenyl acetate, and a compound with a longer g.l.c. retention time. Fraction (vi), crystallised (twice) from petroleum, yielded colourless 5,8-di-*t*-butyl-1,4-dihydro-naphthalene-1,4-endoxide (0.086g.), m.p.  $114-5^{\circ}$ . (Found: C, 84.3; H, 9.5.  $C_{18}H_{24}O$  requires C, 84.3; H, 9.4%). The yield of the endoxide was determined by g.l.c. (Table 4, p. 164). N.m.r. spectrum: see Appendix. I.r. (Nujol): 1125 (C-O-C) and  $725\text{ cm}^{-1}$  (cis CH=CH).



TABLE 4Reactions of 2,5-Di-t-butyl-N-nitrosoacetanilide

Product	Yield (m/100m of nitrosamide) by g.l.c.			
	Reaction H.1	H.2	H.3	H.4
p-Di-t-butylbenzene	7.8	8.4	5.1	4.1
Biphenyl	1.3	< 0.4	< 0.4	-
2,5-Di-t-butylphenyl acetate	79.0	76.9	53.1	63.1
5,8-Di-t-butyl-1,4-dihydronaphthalene-1,4-endoxide			-	29.7

2,5-Di-t-butylbiphenyl (0.5m/100m would have been detected) was absent from reactions H.1, H.2 and H.3; 2,5-di-t-butylphenol (1.0) was absent from reactions H.1 and H.2; 2,5-di-t-butyl-acetanilide (0.9) was absent from all reactions.

Quantitative measurements were made on 2% NPGS, 130° and 158° (reactions H.1, H.2 and H.3) or 2% NPGS, 183° (reaction H.4); and on 10% SIL at 172° (reactions H.1 and H.2) or 189° (reaction H.3) or 158° (reaction H.4).



# I Reactions of 1,4-Di-t-butyl-2,5-di-(N-nitrosoacetamido)benzene

In all experiments except I.1(b), the dinitrosamide was prepared from 2,5-di-t-butyl-p-phenylenediamine (see Section VII).

An authentic specimen of 2,5-di-t-butylresorcinol diacetate could not be prepared. A mixture of this with 2,5-di-t-butylhydroquinone diacetate was isolated in experiment J.3, and since an authentic specimen of the latter was available, the mixture of diacetates could be used to determine the g.l.c. retention time of 2,5-di-t-butylresorcinol diacetate. The isomers, which were resolved on NPGS capillary,  $190^{\circ}$ , were assumed to give an equal response to a flame-ionisation detector.

Biphenyl and 2,5-di-t-butylphenyl acetate were not resolved on 10% CAR, but could be separated on CAR capillary,  $195^{\circ}$ .

The extreme insolubility of 1,4-diacetamido-2,5-di-t-butylbenzene ensured that, were it formed, it would be precipitated from the reaction mixture.

## 1. Decomposition in Benzene

(a) The dinitrosamide (4.68g., 12.9 mmoles) in benzene (39.5g., 0.507 mole) was stirred at  $48^{\circ}$  for 15.5 hr., gradual decomposition occurring. The mixture was boiled under reflux for 1 hr. and allowed to cool, when no solid was deposited. A sample of the brown solution was examined by g.l.c. (Table 5, p. 171) with bibenzyl as internal standard.

(b) Impure 1,4-di-*t*-butyl-2,5-di-(N-nitrosoacetamido)-benzene (3.16g., 8.71 mmoles, prepared from the diamide, was allowed to decompose in benzene (26.4g., 0.348 mole) at the reflux temperature. A white solid (0.247g.) was filtered off from the cooled reaction mixture and identified by its i.r. spectrum and m.p. (above 360°) as 1,4-diacetamido-2,5-di-*t*-butylbenzene (0.813 mmole). The filtrate was examined by g.l.c. (10% APL, 192°) and was found to contain the same products, in the same ratio, as were detected in (a) above.

The bulk (7.51 mmoles impure dinitrosamide) of the filtrate was distilled to give: (i) a colourless liquid, b.p. 80°, (ii) a liquid (trace), bath temp. to 55°/13 mm., (iii) a red sublimate (0.369g.), bath temp. to 180°/0.1 mm., and (iv) a black residue (1.76g.). Fraction (iii), crystallised from benzene, afforded colourless 2,5-di-*t*-butylhydroquinone diacetate (0.160g., 0.523 mmole, 7.1m/100m.; crude, 16.1m/100m), m.p. and mixed m.p. 175-6°. The i.r. spectrum was identical to that of the authentic diacetate.

The residue (iv) was chromatographed on alumina (170g.). Elution with solvents of increasing polarity, from benzene to methanol, gave 67 x 80 ml. fractions. The first 18 contained no appreciable material; the remainder gave only oils, tars or glasses from which no sharp-melting

products could be isolated. Examination of the major fractions by t.l.c. and i.r. spectroscopy did not permit identification of any component.

## 2. Reaction with Anthracene in Benzene

1,4-Di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene (6.80g., 18.8 mmoles) was allowed to decompose in a suspension of anthracene (10.1g., 56.3 mmoles) in benzene (65.1g., 0.835 mole) at 42° for 15 hr. and at the reflux temperature for 1 hr. Unreacted anthracene (8.72g., 49.0 mmoles) was filtered off from the cold reaction mixture and washed with benzene. A sample of the combined filtrate and washings was examined by g.l.c. (Table 5, p.171 ) with trans-stilbene as internal standard. Estimation of the quantity of anthracene in the filtrate (3.83 mmoles) allowed the amount consumed (18.6m/100m) to be computed.

The major portion (15.25 mmoles dinitrosamide) of the filtrate was distilled to give: (i) a colourless liquid, b.p. 79-81°, (ii) an orange sublimate (1.83g.), bath temp. to 180°/0.1 mm., and (iii) a residue (2.97g.). Fraction (ii) was dissolved in chloroform, methanol added, and the precipitated anthracene filtered off. The filtrate deposited large crystals, some of which were picked out and recrystallised from benzene to give 2,5-di-*t*-butylhydroquinone diacetate, m.p. and mixed m.p. 173-4°.

The residue (iii) was dissolved in xylene (25 ml.) and heated with maleic anhydride (1.75g.) and sodium hydroxide solution as in experiment H.3 (p. 161). The resulting solid was chromatographed on alumina (180g.). Elution with solvents of increasing polarity, from petroleum to benzene-ether (4:1), gave 44 x 85 ml. fractions which did not fluoresce in u.v. light, and contained very little material. The next 11 fractions were weakly fluorescent; on evaporation, each gave a brown tar (total 0.478g.). More polar solvents, to methanol, yielded tars or glasses. Representative fractions were examined by t.l.c., and by i.r. and n.m.r. spectroscopy. All contained at least two components, none of which could be isolated or identified. 6,13-Di-*t*-butyl-5,7,12,14-tetrahydro-5,14:7,12-di-o-benzenopentacene was not detected.

### 3. Decomposition in Furan

1,4-Di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene (9.76g., 27.0 mmoles) was allowed to decompose in furan (58.0g., 0.850 mole) at the reflux temperature for 17 hr., and a portion of the resulting solution was examined by g.l.c. (Table 5, p.171) with fluorene as internal standard.

The bulk (22.2 mmoles dinitrosamide) of the deep red reaction mixture gave on distillation: (i) a liquid, b.p. 32°, (ii) a liquid (0.737g.), b.p. 36-40°/14 mm., (iii) a white sublimate (0.048g.), bath temp. to

120°/0.3 mm., (iv) a yellow oily solid (0.616g.), b.p. 120°/0.2 mm., and (v) an orange oily solid (1.30g.), b.p. 120-35°/0.2 mm. No further distillate or sublimate was obtained at a pressure of less than  $10^{-3}$  mm. and a bath temp. to 220°. A black residue (3.67g.) remained. The fractions were examined by g.l.c. (2% NPGS, 80° and 120° programmed to 210°). Fraction (ii) was largely acetic acid (12.3 mmoles, 55m/100m) and (iv) contained 12 components, the major one having a retention time equal to that of 2,5-di-*t*-butylhydroquinone diacetate.

Fraction (v), which contained two principal components, was crystallised repeatedly from petroleum-benzene to give impure 2,5-di-*t*-butylhydroquinone diacetate (0.134g.), m.p. and mixed m.p. 169-71°. The i.r. spectrum contained absorptions at 3310 and 1660  $\text{cm}^{-1}$  not present in the spectrum of the authentic diacetate, but the n.m.r. spectra were indistinguishable. The other component of this fraction could not be isolated.

Chromatography of the distillation residue on alumina (160g.) yielded only intractable oils and tars.

#### 4. Decomposition in trans-1,2-Dichloroethylene

1,4-Di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene (7.45g., 20.6 mmoles) was allowed to decompose in trans-1,2-dichloroethylene (78.5g., 0.810 mole) at 30-40° for 17 hr. and at the reflux temperature for 1 hr.

The major part (18.9 mmoles of dinitrosamide) of the brown solution was distilled to yield: (i) a liquid, b.p. 48-53°, (ii) a liquid (1.81g.), b.p. 54-76°, (iii) a liquid (0.046g.), bath temp. to 100°/18 mm., (iv) a red solid (1.54g.), bath temp. to 180°/0.1 mm., and (v) a black residue (3.55 g.). Fraction (iv) was seen by g.l.c. examination (2% NPGS, 192°) to contain 6 components, the two principal ones being those with the longest retention times. A portion (12.2 mmoles dinitrosamide) of this fraction was applied to silica gel t.l.c. plates which were developed with petroleum-benzene (4:1). The component with the longest g.l.c. retention time had  $R_f$  0.0, and was identified as 2,5-di-*t*-butylhydroquinone diacetate (crude, 0.241g., 0.787 mmole, 6.5m/100m), m.p. 174-5°, mixed m.p. 173-4°. The other major component, with  $R_f$  0.27, was identified after crystallisation from methanol as 4-chloro-2,5-di-*t*-butylphenyl acetate (crude, 0.177g., 0.627 mmole, 5.1m/100m) m.p. 100-101°. (Found: C, 67.8; H, 8.55; Cl, 12.55.  $C_{16}H_{23}ClO_2$  requires C, 67.95; H, 8.2; Cl, 12.5%).

N.m.r. ( $CDCl_3$ ):  $\tau$  2.69 (s,  $H_6$ ), 3.01 (s,  $H_3$ ), 7.70 (Me), 8.56 (t-Bu) and 8.69 (t-Bu).

I.r. (Nujol): 1760  $cm^{-1}$  (C=O).

No other single components could be isolated by t.l.c.

A sample of the original reaction mixture was examined by g.l.c. (Table 5, p. 171) with trans-stilbene as internal standard.



TABLE 5Reactions of 1,4-Di-t-butyl-2,5-di-(N-nitrosoacetamido)benzene

Product	Yield (m/100m of dinitrosamide) by g.l.c.			
	Reaction I.1	I.2	I.3	I.4
Acetic acid	38	63	101	70
Biphenyl	1.2	< 0.1	-	-
2,5-Di-t-butylphenyl acetate	1.6	1.2	2.7	2.6
2,5-Di-t-butylhydroquinone diacetate	15.5	12.9	8.5	15.2
2,5-Di-t-butylbiphenyl	1.7	1.0	-	-
2,5-Di-t-butylphenol	0.25	< 0.1	1.3	< 0.1
4-Chloro-2,5-di-t-butylphenyl acetate	-	-	-	6.8

p-Di-t-butylbenzene (0.2m/100m would have been detected) and 2,5-di-t-butylresorcinol diacetate (0.5) were absent from all reactions; 5,8-di-t-butyl-1,4-dihydronaphthalene-1,4-endoxide (0.2) was absent from reaction I.4.

Quantitative measurements were made on 10% CAR, 200°, 10% APL, 200°, and NPGS capillary, 190°.



J Reactions of 2,5-Di-t-butyl-1,3-di-(N-nitrosoacetamido)benzene

1. Decomposition in Benzene

1,3-Diacetamido-2,5-di-t-butylbenzene (0.210g., 0.690 mmole) was nitrosated and the reaction mixture poured into iced 10% potassium hydrogen carbonate solution (30 ml.). The yellow oily solid which separated was extracted with benzene (15,10, 2 x 5 ml.) and the combined extracts were stirred with magnesium sulphate for 30 min. and phosphorus pentoxide for 5 min., the temperature being kept below 5°. Solid matter was filtered off and washed with benzene, giving a solution of the dinitrosamide (assumed 0.690 mmole) in benzene (40 ml.). Rapid darkening was observed when the solution was stirred at 42°. After 16 hr., the mixture was heated at the reflux temperature for 1 hr., and was concentrated by distillation.

A sample of the reaction product was examined by g.l.c. (10% APL, 192°; NPGS capillary, 190°) with bibenzyl as internal standard, and the following were detected: p-di-t-butylbenzene (0.3m/100m), biphenyl (6.8), 2,5-di-t-butylphenyl acetate (4.8), 2,5-di-t-butylhydroquinone diacetate (0.4) and 2,5-di-t-butylresorcinol diacetate (0.6). 2,5-Di-t-butylphenol (0.07m/100m would have been detected) and 2,5-di-t-butylbiphenyl (0.1) were absent.

2. Decomposition in Cyclohexane

A dry solution of 2,5-di-t-butyl-1,3-di-(N-nitroso-

acetamido)benzene (0.431g., 1.42 mmoles) in cyclohexane (140 ml.), prepared by a similar procedure to that above, was stirred at 42° for 15 hr. and at the reflux temperature for 1 hr. After concentrating by distillation, a sample of the reaction mixture was examined by g.l.c. (10% APL, 192°; NPGS capillary, 190°) with bibenzyl as internal standard, and was found to contain: *p*-di-*t*-butylbenzene (1.2m/100m), 2,5-di-*t*-butylphenyl acetate (13.7), 2,5-di-*t*-butylhydroquinone diacetate (1.2) and 2,5-di-*t*-butylresorcinol diacetate (2.0). 2,5-Di-*t*-butylphenol (0.3m/100m would have been detected) was absent.

### 3. Attempted Isolation of 2,5-Di-*t*-butylresorcinol Diacetate

The reaction mixtures (including g.l.c. samples) from the above two reactions were combined and subjected to preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% NPGS on celite at 215°). The material corresponding to a single peak with retention time 17 min. was collected, affording an oily yellow solid (0.017g.) which was found by g.l.c. examination (NPGS capillary, 190°) to contain two principal components, having retention times of 16 min. (ca. 40%) and 16.6 min. (ca. 60%). Authentic 2,5-di-*t*-butylhydroquinone diacetate had retention time 16.0 min.

N.m.r. (CDCl<sub>3</sub>):  $\tau$  2.99 (s) and 3.16 (s) (together ca. 2H);  
7.67 (s) and 7.70 (s) (together ca. 6H);

8.60 (s), 8.67 (s) and 8.72 (s)

(total ca. 18H; ratio ca. 7:12:7).

Crystallisation of the mixture from ethanol at  $-40^{\circ}$  yielded the component with the shorter retention time (0.005g.), which had an i.r. spectrum identical to that of 2,5-di-*t*-butylhydroquinone diacetate. The crystallisation mother-liquor was evaporated and the residue heated in a sublimation tube at  $180^{\circ}$  (block temp.)/0.02 mm. to give a viscous brown oil, which was dissolved in petroleum (0.4 ml.). When the solution was cooled to  $-60^{\circ}$ , a brown solid (0.002g.), consisting of ca. 70% of the component with the longer retention time, was deposited. This material was examined by mass spectroscopy (see p. 249).

## K Reactions of 4-Acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide

### 1. Decomposition in Benzene

The nitrosamide (7.02g., 21.0 mmoles) was allowed to decompose in benzene (65.5g., 0.84 mole) at  $42^{\circ}$  for 17 hr., when rapid darkening of the solution was observed; and at the reflux temperature for 1 hr. A sample of the resulting solution was examined by g.l.c. (Table 6, p. 177) with bibenzyl as internal standard.

The bulk (18.1 mmoles nitrosamide) of the reaction mixture gave on distillation: (i) a liquid, b.p.  $79-95^{\circ}$ ,

(ii) a yellow sublimate (0.099g.), bath temp. to  $110^{\circ}/0.05$  mm., (iii) an orange solid (0.209g.), b.p.  $70-80^{\circ}/0.05$  mm., (iv) a red oil (0.300g.), b.p.  $80-100^{\circ}/0.05$  mm., and (v) a residue. G.l.c. examination (10% PEGA,  $199^{\circ}$ ) indicated that fractions (ii) and (iii) contained comparable amounts of biphenyl, 2,5-di-*t*-butylphenyl acetate, 2,5-di-*t*-butylphenol, and an unidentified product; while fraction (iv) contained, in addition to these, 2,5-di-*t*-butylhydroquinone diacetate. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% NPGS on celite; temperature programme,  $145^{\circ}$  rising at  $1^{\circ}/\text{min.}$  for 26 min., then  $24^{\circ}/\text{min.}$  to  $215^{\circ}$ , then isothermal) of fractions (ii) and (iii) allowed isolation of a sample of the unknown component, contaminated with biphenyl (ca. 10%) from which it was only partially resolved. Crystallisation from petroleum yielded yellow needles of 2,5-di-*t*-butyl-*p*-benzoquinone, m.p.  $152-3^{\circ}$ , mixed m.p.  $153-3\frac{1}{2}^{\circ}$ . The i.r. spectrum was identical to that of the authentic quinone. N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  3.48 (s, 2H) and 8.70 (s, 18H, *t*-Bu).

In a control experiment a solution of 2,5-di-*t*-butylphenyl acetate (1.0 mmole) in benzene (0.2 mole) containing acetic acid (5.0 mmoles) and water (2% by weight of the benzene) was boiled under reflux for 4 hr. G.l.c. examination (NPGS capillary,  $190^{\circ}$ ) showed that less than 0.1% of the ester had been hydrolysed to 2,5-di-*t*-butylphenol.

## 2. Decomposition in Cyclohexane

(a) 4-Acetoxy-2,5-di-*t*-butyl-N-nitrosoacetanilide (0.834g., 2.50 mmoles) decomposed slowly in suspension in cyclohexane (10.5g., 0.125 mole) at 42°. After 16 hr. the red solution was boiled under reflux for 1 hr. and a sample was examined by g.l.c. (Table 6, p.177) with bibenzyl as internal standard.

(b) From a similar reaction of the nitrosamide (5.86g., 17.5 mmoles) in cyclohexane (73.5g., 0.877 mole) there were obtained by distillation: (i) a liquid, b.p. 77-81°, (ii) an orange solid (0.815g.), b.p. 65-140°/0.05 mm., (iii) a red solid (0.764g.), b.p. 140-60°/0.05 mm., and (iv) a brown residue (2.83g.). Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% NPGS on celite at 205°) of fraction (iii) yielded samples of 2,5-di-*t*-butylphenyl acetate, m.p. and mixed m.p. 51-2°; 2,5-di-*t*-butylphenol, m.p. and mixed m.p. 120-21°; and 2,5-di-*t*-butylhydroquinone diacetate, m.p. and mixed m.p. 175-6°. The identities of these components were confirmed by their i.r. (and for the phenol, n.m.r.) spectra.

TABLE 6Reactions of 4-Acetoxy-2,5-di-t-butyl-N-nitrosoacetanilide

Product	Yield (m/100m of nitrosamide) by g.l.c.	
	Reaction K.1	K.2(a)
Acetic anhydride	70-90	50-70
2,5-Di-t-butyl-p-benzoquinone	5.8	2.4
2,5-Di-t-butylphenyl acetate	2.5	8.3
2,5-Di-t-butylphenol	5.1	5.9
2,5-Di-t-butylhydroquinone diacetate	2.2	7.7
Biphenyl	2.7	-

2,5-Di-t-butylresorcinol diacetate [0.02m/100m would have been detected in reaction K.1, 0.2 in reaction K.2(a)] and p-di-t-butylbenzene (0.2) were absent.

Quantitative measurements were made on 10% PEGA, 159° and 199°, and NPGS capillary, 190°. Acetic anhydride was measured approximately on 2% CAR, 45° with o-bromotoluene as internal standard. The i.r. spectra of the nitrosamide used in these experiments contained no absorption at 1830 cm.<sup>-1</sup> (C=O in acetic anhydride).

## I Reactions of p-Acetoxy-N-nitrosoacetanilide

### 1. Decomposition in Benzene

p-Acetoxy-N-nitrosoacetanilide (1.44g., 6.495 mmoles) was allowed to decompose in benzene (20.3g., 0.260 mole) at 38° for 16 hr. and at the reflux temperature for 1 hr. A sample of the reaction mixture was examined by g.l.c. (2% NPGS, 172° and 202°; 8% BDS, 227°) with trans-stilbene as internal standard, and was found to contain 4-acetoxybiphenyl (39.4m/100m) and 4-hydroxybiphenyl (2.0). Hydroquinone monoacetate (0.1m/100m would have been detected), hydroquinone diacetate (0.07), 3-acetoxybiphenyl (0.07) and p-acetoxyacetanilide (0.7) were absent. A further sample was seen by g.l.c. examination (2% NPGS, 106°; 8% BDS, 160°) with naphthalene as internal standard to contain phenyl acetate (2.1m/100m). Phenol (0.3m/100m would have been detected), p-benzoquinone (0.2) and biphenyl (0.3) were absent.

Aniline (1.30 mmoles) was added to a portion (1.22 mmoles nitrosamide) of the reaction mixture, which was then stirred at 40° for 30 min. G.l.c. examination (2% NPGS, 172°) indicated that acetanilide (67m/100m), absent from the original reaction mixture, was now present. The i.r. spectrum of the nitrosamide used in this experiment did not contain a band at 1830 cm.<sup>-1</sup> (C=O in acetic anhydride).



M Reactions of Diphenyl[o-(N-nitrosoacetamido)phenyl]phosphine Oxide

1. Decomposition in Benzene

o-Acetamidophenyldiphenylphosphine oxide (5.40g., 16.1 mmoles) was nitrosated and the reaction mixture poured into iced water (150 ml.). The yellow oil which separated was extracted with benzene (25, 10 ml.) and the extracts were washed with water (40 ml.), 5% potassium hydrogen carbonate solution (40 ml.), and water (40 ml.), and stirred with magnesium sulphate for 45 min. and calcium sulphate for 45 min., the temperature being kept below 5°. Filtration gave a solution of the impure nitrosamide (see Section VII) in benzene (37 g., 0.48 mole), which darkened slowly. When the reaction was complete, a portion (from 11.2 mmoles amide) of the reaction mixture was chromatographed repeatedly on silica gel, giving only oils and tars. One such fraction, crystallised from ether and from light-petroleum (b.p. 60-80°)-benzene (4:1) yielded o-acetamidophenyldiphenylphosphine oxide, m.p. 128-9°, mixed m.p. 127.5-8°. The i.r. and n.m.r. spectra were indistinguishable from those of the authentic amide. T.l.c. examination on silica gel with ether-methanol (19:1) suggested that the amide was a major component of most of the chromatography fractions. Diphenyl(o-hydroxyphenyl)phosphine oxide and o-acetoxyphenyldiphenylphosphine oxide could not,

with certainty, be detected. A portion of the original reaction mixture was boiled with 10% sodium hydroxide solution and the aqueous phase separated, washed with benzene and ether, acidified, and extracted with chloroform. The extract, on evaporation, gave a red tar which could not be crystallised. T.l.c. examination revealed three principal components, one of which had the same  $R_F$  value as diphenyl(o-hydroxyphenyl)-phosphine oxide.

## 2. Reaction with Anthracene in Benzene

Anthracene (4.26g., 24.0 mmoles) was added to a dry benzene solution (47 ml.) of the product from the nitrosation of o-acetamidophenyldiphenylphosphine oxide (4.01g., 12.0 mmoles), and the mixture stirred at 45° for 12 hr. and boiled. Part (from 11.6 mmoles amide) of the reaction mixture was chromatographed on silica gel (290g.). Anthracene (3.07g.) was removed in benzene, and the column was then eluted with ether containing an increasing proportion of methanol (0-100%), yielding 52x 200 ml. fractions which were examined by t.l.c. on silica gel with ether-methanol (19:1). Fractions 1-13 contained two fluorescent components ( $R_F$  0.55 and 0.68); fractions 14-45 contained the slower-moving of these, and also a substance with the same  $R_F$  value as o-acetamidophenyldiphenylphosphine oxide. Later fractions were very complex. Fractions 14-23 formed a yellow tar (0.698g.)

which was boiled with ether to give a powder (0.178g.).

Crystallisation from carbon tetrachloride afforded strongly fluorescent pale yellow needles (0.124g.), m.p. 228-9°.

(Found: C, 83.2; H, 5.1; P, 7.6; residue, 1.15%.  $M^+$ , 454).

N.m.r. ( $CDCl_3$ ):  $\tau$  1.87-3.11 (very complex).

I.r. (Nujol): 1200  $cm^{-1}$  (P=O).

$\lambda_{max.}$  (log  $\epsilon$  for  $M = 454$ ) in methanol: 224 (4.54), 253.5 (4.85),  
316 (3.16), 332 (3.43), 348 (3.73),  
365.5 (3.92) and 384.5  $m\mu$  (3.87).

This compound, probably 9-(o-diphenylphosphinylphenyl)anthracene (0.27 mmole, 2.2m/100m of amide), had  $R_F$  0.55. ( $C_{32}H_{23}OP$  requires C, 84.6; H, 5.1; P, 6.8%.  $M^+$ , 454).

The remaining chromatography fractions were combined, and together with the mother-liquors from the crystallisation of fractions 14-23, were dissolved in xylene (25 ml.) and boiled with maleic anhydride (2.2g.) and sodium hydroxide solution as in experiment H.3 (p. 161). The resulting tar was chromatographed on alumina (210g.). Elution with ether-methanol (9:1) afforded a brown tar (1.75g.) which was leached with boiling ether, leaving a pale brown solid residue. This material, crystallised twice from carbon tetrachloride, afforded pale brown needles (0.061g.), m.p. 227-8°. (Found: C, 82.5; H, 5.0; P, 9.7; residue 1.5%.  $M^+$  454).

N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  ca. 2.45 (unresolved multiplet), ca. 3.13 (unresolved multiplet), 3.81 (s) and 4.56 (s). The integrals were in the approximate ratio 13:8:0.8:0.8.

I.r. (Nujol): 1200, 1180  $\text{cm}^{-1}$

$\lambda_{\text{max}}$ . (log  $\epsilon$  for  $M = 454$ ) in methanol: 226.5 (4.39), 251sh (3.41), 260 (3.36), 265 (3.46), 272 (3.57), 284 (3.60) and 291 m $\mu$  (3.63).

The product was possibly (impure) 1-diphenylphosphinyltriptycene (0.14 mmole, 1.2m/100m). ( $\text{C}_{32}\text{H}_{23}\text{OP}$  requires C, 84.6; H, 5.1; P, 6.8%.  $M^+$ , 454).

## N Reactions of Diethyl o-(N-Nitrosoacetamido)phenylphosphonate

### 1. Decomposition in Benzene

The nitrosamide (1.42g., 4.74 mmoles) was dissolved in benzene (7.80g., 0.100 mole) and the solution stirred at 40-50°, when slow decomposition occurred during 36 hr. The mixture was slowly heated to the reflux temperature, and boiled for 2 hr. A sample of the reaction product was examined by g.l.c. (3% CAR, 173°; 2% NPGS, 172°) with phenanthrene as internal standard, and was found to contain diethyl phenylphosphonate (4.6m/100m), diethyl o-acetoxyphenylphosphonate (7.7), diethyl m-acetoxyphenylphosphonate (1.05), diethyl o-acetamidophenylphosphonate (3.1), diethyl

2-biphenylphosphonate (22.8), and biphenyl (trace, less than 0.4). Diethyl o-hydroxyphenylphosphonate (0.3m/100m would have been detected) was absent. The identities of these products were confirmed on 3% QF-1, 155° and 170°.

APPENDIX OF  $^1\text{H}$  N.M.R. SPECTRAL DATA1,4-Dihydronaphthalene-1,4-endoxides ( $\tau$  values)

Substituents	Aromatic <sup>(a)</sup>	Olefinic <sup>(b)</sup>	Bridge-head <sup>(c)</sup>	Alkyl <sup>(d)</sup>
1) None		3.10	4.48	-
2) 5-t-Bu	2.88-3.28	3.08	4.01, 4.51	8.66
3) 6-t-Bu	2.65-3.22	3.05	4.46	8.71
4) 5,8 t-Bu	3.06	2.91	3.83	8.62
5) 6-Br; 5,8 t-Bu <sup>(e)</sup>	2.80	3.02	3.78, 4.04	8.42, 8.66
6) 1,4 Me	3.12	3.40	-	8.23

Data for unsubstituted endoxide supplied by Dr. R.K. Mackie.

Solvent:  $\text{CCl}_4$  (spectra 2,5);  $\text{CDCl}_3$  (spectra 3,4,6).

(a) 3H, complex (2,3); 2H, singlet (4); 1H, singlet (5); 4H AA'BB' (6).

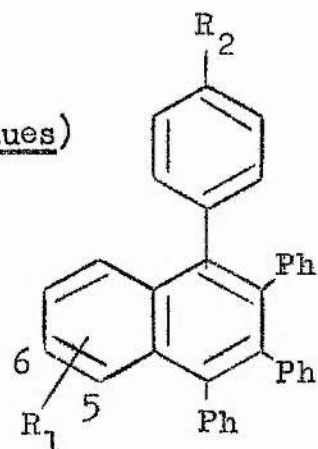
(b) 2H, broad singlet giving multiplet on expansion (1-5) or 2H, sharp singlet.(6).

(c) 2H, broad singlet giving multiplet on expansion (1,3,4) or two 1H broad singlets giving multiplets on expansion (2,5).

(d) Singlet.

(e) Irradiation at 3.02 simplified multiplets at 3.78 and 4.04.

Irradiation at 3.78 or 4.04 simplified multiplet at 3.02.

1-Aryl-2,3,4-triphenylnaphthalenes ( $\tau$  values)

	$R_1$	$R_2$	Naphthalene <sup>(a)</sup>	Other aromatic		<i>t</i> -Butyl <sup>(d)</sup>
1)	H	H	2.20-2.85	2.83 <sup>(b)</sup>	3.22 <sup>(c)</sup>	-
2)	6- <i>t</i> -Bu	H	2.21-2.50	2.77	3.15	8.74
3)	6-Cl	H	2.28-2.72	2.82	3.19	-
4)	5- <i>t</i> -Bu	H	2.24-2.84	2.91, 3.10	3.30	9.02
5)	5-Cl	H	2.29-2.72	2.82, 2.90	3.20	-
6)	H	<i>p</i> - <i>t</i> -Bu	2.10-2.85	2.78	3.15	8.72

Solvent:  $\text{CDCl}_3$  (spectra 2,3,5,6);  $\text{CCl}_4$  (spectra 1,4)

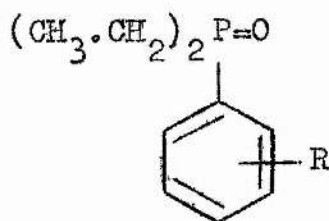
(a) Complex.

(b) One 10H singlet (1,2,3); two 5H singlets (4,5); one 9H singlet (6).

(c) One 10H singlet (1-4,6); two absorptions (total 10H) separated by 1 c./sec. (5).

(d) 9H, singlet.



Diethyl Arylphosphonates ( $\tau$  values)

Group R	Aromatic <sup>(a)</sup>	$-\text{CH}_2-$ <sup>(b)</sup>	$\text{CH}_3-$ <sup>(c)</sup>	$\text{R}$ <sup>(d)</sup>
<u>o</u> -Ph	1.70-3.35	6.17	8.91	See (a)
<u>o</u> -NO <sub>2</sub>	1.68-2.52	5.87	8.66	—
<u>o</u> -NH <sub>2</sub>	2.38-3.62	5.94	8.70	4.51
<u>o</u> -NHAc	1.10-3.18	5.91	8.67	-0.66; 7.86
<u>o</u> -OH	2.40-3.38	5.95	8.70	-0.21
<u>o</u> -OAc	1.95-3.14	6.00	8.73	7.76
<u>m</u> -OH	2.15-3.24	5.94	8.70	0.58
<u>m</u> -OAc	2.16-3.05	5.98	8.71	7.78

Solvent: CCl<sub>4</sub> for all spectra.

(a) 4H, complex; and for o-Ph, 2.63 (s, Ph).

(b) 1:4:6:4:1 pentet due to overlap of two 1:3:3:1 quartets.

$J_{(\text{CH}_2)-(\text{CH}_3)} \doteq J_{(\text{CH}_2)-(\text{P})} \doteq 7\text{c./sec.}$  (average value).

(c) 1:2:1 triplet.  $J_{(\text{CH}_2)-(\text{CH}_3)} \doteq 7\text{c./sec.}$  (average value).

(d) Singlet, broadened when H attached directly to N.

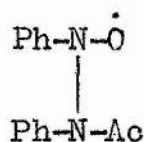
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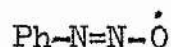
REACTIONS OF ACETYLARYLNITROSAMINES

Grieve and Hey<sup>7</sup> initiated a systematic investigation of the reactions of acetylarylnitrosamines in 1934, and since that time the mechanism of the decomposition of N-nitrosoacetanilide, particularly in aromatic solvents, has continuously attracted attention. The major advances in the development of mechanistic ideas unto the present day have been traced in the Introduction to this thesis. Recognition of an aryl radical, derived from the covalent arenediazoacetate, as the reactive entity in arylation reactions was followed by the discovery that the rate-determining step is rearrangement of the nitrosamide to the trans-diazooester. Extensive investigations culminated in the suggestion of a non-ionic mechanism for the rearrangement, although the possible importance of heterolytic processes, particularly in azo coupling reactions and in the replacement of substituents during the decomposition of certain acylarylnitrosamines, was not overlooked. An abundance of evidence for the generation of a phenyl radical in the decomposition of N-nitrosoacetanilide was in marked contrast to the dearth of evidence for the simultaneous formation of an acetoxy radical. The mechanism proposed by Rüchardt and Freudenberg<sup>125</sup> in 1964 (p.57) not only rationalised the formation of acetic acid as a non-radical process, but also provided a plausible explanation of other characteristic features of

the reactions of acetylarlylnitrosamines. Although Perkins and his co-workers<sup>152</sup> have recently shown that the e.s.r. spectrum observed during the decomposition of N-nitrosoacetanilide in benzene is probably that of the nitroxide radical (XVII) rather than the phenyl diazotate radical (XVIII),



(XVII)



(XVIII)

the consequent modifications (p.59) to Rüchardt and Freudenberg's theory do not invalidate its fundamental concepts. Except where the modified scheme appears to be of direct relevance, the results of the present investigation will, for convenience, be discussed in terms of the mechanism originally proposed.

The decomposition of o-*t*-butyl-N-nitrosoacetanilide in benzene was first studied by Cadogan, Hey and Williams,<sup>153</sup> who found that little 2-*t*-butylbiphenyl was formed, the major product being a mixture of isomeric *t*-butylphenyl acetates, subsequently shown by Cadogan and Hibbert<sup>8</sup> to contain only the o- and m- isomers. The formation of m-*t*-butylphenyl acetate, together with isolation of 1-*t*-butyltritycene from the decomposition in the presence

of anthracene, was thought to indicate aryne participation in the reactions of o-*t*-butyl-N-nitrosoacetanilide. This anomalous behaviour was attributed to the bulk of the o-substituent.

Brydon and Cadogan's investigation<sup>155</sup> of the reactions of a number of o-substituted derivatives of N-nitrosoacetanilide failed to reveal any which resembled closely the decomposition of o-*t*-butyl-N-nitrosoacetanilide, although the formation of 3-acetoxybiphenyl (4.5m/100m) and m-carbethoxyphenyl acetate (2.1m/100m) suggested some aryne participation in the decompositions of 2-(N-nitrosoacetamido)biphenyl and o-carbethoxy-N-nitrosoacetanilide. These same workers<sup>155</sup> also observed that the decomposition of N-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone gave a much reduced yield of biphenyl, the major product being the benzyne adduct,\* 1,2,3,4-tetraphenylnaphthalene (24.7m/100m). The question therefore arose whether the absence of aryl acetates from the products of decomposition of an acetylarlylnitrosamine was, in fact, indicative of non-participation by an aryne intermediate.

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\* In reactions with 2,3,4,5-tetraphenylcyclopentadienone the term 'adduct' will be used to refer to the isolated product, i.e. the 1,4-addition product after loss of carbon monoxide (see p.22).

Chloro-N-nitrosoacetanilides

Haworth and Hey<sup>196</sup> reported that o-chloro-N-nitrosoacetanilide [m.p. 59° (decomp.)] in benzene eliminated oxides of nitrogen with the formation of o-chloroacetanilide. More recently, however, a compound [m.p. 46-7° (decomp.)] was obtained from the nitrosation of o-chloroacetanilide which decomposed in benzene to yield 2-chlorobiphenyl (36m/100m); o-chlorophenyl acetate was reported to be absent from the products.<sup>155</sup> The nitrosamide used in the present investigation, discussed below, had m.p. 46-7° (decomp.).

5-Chloro-1,2,3,4-tetraphenylnaphthalene could not be detected among the products of decomposition of o-chloro-N-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone, while it was possible to show (g.l.c.) that when phenyl azide was the arynophile, the amount of adduct that would result from 3-chlorobenzyne did not exceed 0.05m/100m. Since 3-chlorobenzyne generated by diazotisation of 3-chloroanthranilic acid formed the expected adducts with both 2,3,4,5-tetraphenylcyclopentadienone and phenyl azide, it could be inferred that an aryne intermediate did not participate in the decomposition of o-chloro-N-nitrosoacetanilide in benzene.

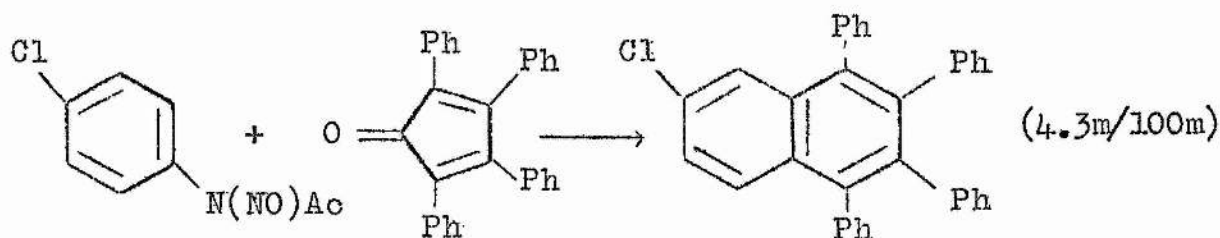
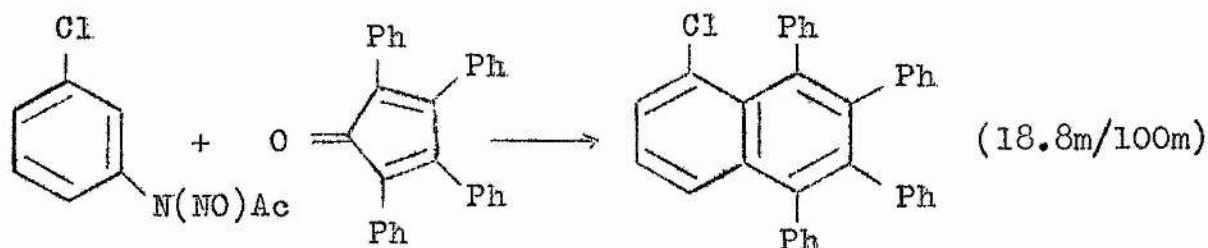
The yield of 2-chlorobiphenyl (35.9m/100m) from o-chloro-N-nitrosoacetanilide in benzene containing phenyl

azide was the same as that reported for the decomposition in pure benzene,<sup>155</sup> while the detection of o-chloroacetanilide (24.1m/100m) was consistent with Haworth and Hey's observation<sup>196</sup> that denitrosation could occur. 2-Acetoxybiphenyl was not detected, in agreement with Suschitzky's suggestion<sup>142,143</sup> that fluorine alone among the halogens is sufficiently labile to be displaced from the intermediate arenediazonium acetate during the decomposition of an acetylarlylnitrosamine. Certain differences were apparent in the reaction with 2,3,4,5-tetraphenylcyclopentadienone: the yields of 2-chlorobiphenyl (28.4m/100m) and o-chloroacetanilide (6.0m/100m) were lower than with phenyl azide, while 2-acetoxybiphenyl (3.9m/100m) and o-chlorophenyl acetate (0.4m/100m) were formed. The participation of 2,3,4,5-tetraphenylcyclopentadienone in the reaction, albeit not as an arynophile, was further indicated by the consumption of an appreciable quantity (33.7m/100m nitrosamide) of the diene.

The decomposition of both m- and p-chloro-N-nitrosoacetanilide in benzene containing 2,3,4,5-tetraphenylcyclopentadienone resulted in markedly lower yields of the corresponding chlorobiphenyl (2.8 and 5.25m/100m) and acetoxybiphenyl (0.1 and 0.6m/100m) than were obtained from the o-isomer. The formation of small amounts of m- and p-chlorophenyl acetates (0.5 and 0.9m/100m) may have



been, as with the o-nitrosamide, a consequence of the presence of the diene. In contrast, however, to o-chloro-N-nitrosoacetanilide, the m- and p-isomers formed aryne adducts with 2,3,4,5-tetraphenylcyclopentadienone:

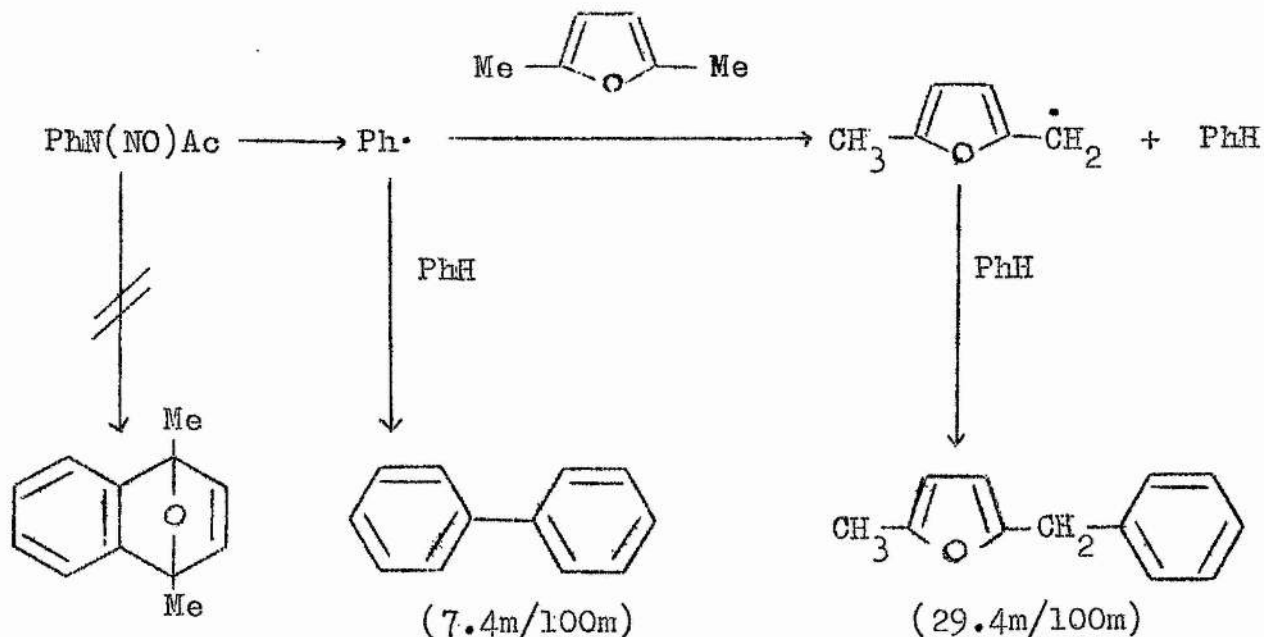


6-Chloro-1,2,3,4-tetraphenylnaphthalene was not detected in the reaction of m-chloro-N-nitrosoacetanilide.

#### N-Nitrosoacetanilide

Although Brydon and Cadogan<sup>155</sup> isolated 1,2,3,4-tetraphenylnaphthalene from the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in benzene, they noted

that triptycene was not formed in the reaction with anthracene. Since it seemed possible that Brydon and Cadogan's result might merely reflect the inefficiency of anthracene as a benzyne scavenger, N-nitrosoacetanilide was allowed to decompose in benzene in the presence of three very reactive arynophiles. 1-Phenylbenzotriazole was not detected among the products of the reaction with phenyl azide, the only compounds isolated being biphenyl (31.7m/100m) and p-terphenyl; and no 1,4-dihydro-naphthalene-1,4-endoxide resulted from the reaction with furan. Although the amount of benzene exceeded that of furan by a factor of six, the yield of biphenyl (16.9m/100m) was appreciably less than the yield of 2-phenylfuran (22.6m/100m), illustrating the ease of homolytic substitution at position two in furan. Other workers<sup>201</sup> have observed that the competitive phenylation of furan and benzene yields approximately fifteen times as much 2-phenylfuran (and none of the 3-isomer) as biphenyl. Even greater selectivity was exhibited by the phenyl radicals in the reaction of N-nitrosoacetanilide with 2,5-dimethylfuran in benzene, the major product being 2-benzyl-5-methylfuran:



The benzyne adduct, 1,4-dimethyl-1,4-dihydronaphthalene-1,4-endoxide was not detected.

The results from the experiments with N-nitrosoacetanilide and the chloro-N-nitrosoacetanilides left little room for doubt that an intermediate displaying some arynoid properties could be formed in the decomposition of other acetylarlylnitrosamines as well as o-t-butyl-N-nitrosoacetanilide. Since this intermediate had evidenced itself only in the presence of 2,3,4,5-tetraphenylcyclopentadienone, it was reasonable to question whether it was, in fact, a true aryne. A fresh investigation of the decomposition of o-t-butyl-N-nitrosoacetanilide, in which 3-t-butylbenzyne had been diagnosed in the absence of an arynophile, and of its m- and p-isomers, was therefore deemed necessary.

t-Butyl-N-nitrosoacetanilides

Decomposition of t-Butyl-N-nitrosoacetanilides in Benzene.— The published information relating to the decomposition of o-t-butyl-N-nitrosoacetanilide was discussed earlier (p.62), while investigations of the reactions of m- and p-t-butyl-N-nitrosoacetanilides have been confined to their application to the synthesis of 3- and 4-t-butylbiphenyls.<sup>153,154</sup> The most significant results from the present investigation of the decomposition of the isomeric t-butyl-N-nitrosoacetanilides in benzene (20m/m of nitrosamide) are reproduced in Table 7 overleaf.

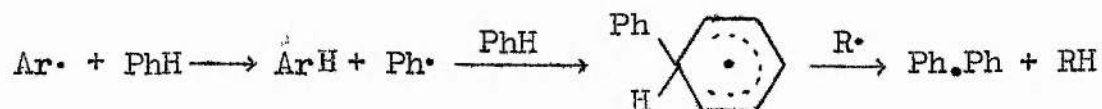
In accord with the observations of other workers<sup>153,154</sup> little 2-t-butylbiphenyl (2.3m/100m) was formed by the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene, although 3- and 4-t-butylbiphenyls (19.4 and 36.4m/100m) were, respectively, the major products from the m- and p-nitrosamides. A low yield of 2-t-butylbiphenyl would result if o-t-butylphenyl radicals were not readily formed from o-t-butyl-N-nitrosoacetanilide, or, if having been formed, they were to react in some way other than by substitution of benzene. While it is tempting to suggest that the bulk of the t-butyl group greatly reduces the amount of substitution, experimental observations do not fully support such an explanation. Thus the decomposition of

TABLE 7Decomposition of t-Butyl-N-nitrosoacetanilides in Benzene

Product	Yield (m/100m nitrosamide)		
	<u>ortho</u>	<u>meta</u>	<u>para</u>
t-Butylbenzene	10.2	4.2	5.9
Biphenyl	3.9	0.3	0.4
<u>o</u> -t-Butylphenyl acetate	37.8	0	0
<u>m</u> -t-Butylphenyl acetate	17.4	7.9	0
<u>p</u> -t-Butylphenyl acetate	0	0	0.5
2-t-Butylbiphenyl	2.3	0	0
3-t-Butylbiphenyl	0	19.4	0
4-t-Butylbiphenyl	0	0	36.4
t-Butylacetanilide	0.3	14.2	5.8
Accountance % of Ar in ArN(NO)Ac	68.0	45.7	48.6

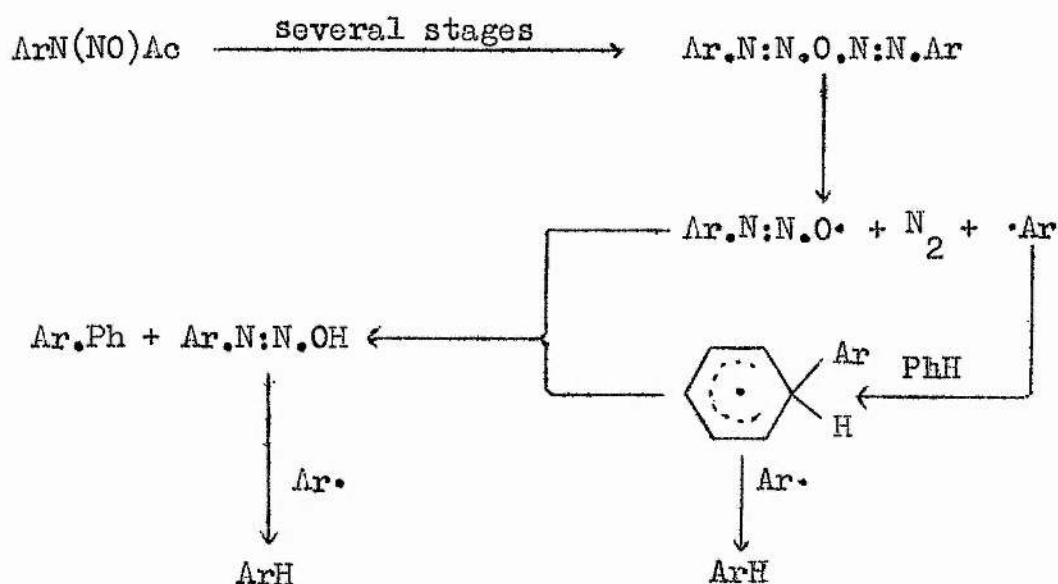
The symbol 0 in this and succeeding Tables indicates that the product was not detected; the limit of detectability is quoted in the Experimental section.

di-m-t-butylbenzoyl peroxide in benzene - a reaction in which steric effects are not great - affords 3-t-butylbiphenyl (65m/100m peroxide) in a yield greater, but only by a factor of two, than that in which 2-t-butylbiphenyl (34m/100m peroxide) is formed from the o-substituted peroxide.<sup>153</sup> In contrast, m-t-butyl-N-nitrosoacetanilide yields eight times as much t-butylbiphenyl as does the o-nitrosamide. Abstraction of hydrogen from the solvent provides an alternative, and less hindered, reaction for o-t-butylphenyl radicals. Although it is not recorded whether t-butylbenzene is formed in the reactions of di-o-t-butylbenzoyl peroxide, it is undoubtedly an important product (10.2m/100m) of the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene. The phenyl radicals released by abstraction of hydrogen would be expected to appear mainly as biphenyl - also a decomposition product (3.9m/100m) of the nitrosamide.



t-Butylbenzene (4.2 and 5.9m/100m) was obtained in smaller, but still significant, yields from m- and p-t-butyl-N-nitrosoacetanilides. In these reactions, however, it was accompanied by minimal amounts of biphenyl (0.3 and 0.4m/100m). Might it be that here there is some species from which hydrogen can be abstracted more readily than

it is from the solvent ? Both of these reactions are essentially normal acylarylnitrosamine arylations; assuming that Rüchardt and Freudenberg's mechanism is operative, two potential hydrogen donors - the arylcyclohexadienyl radical and the arenediazohydroxide - will be present:



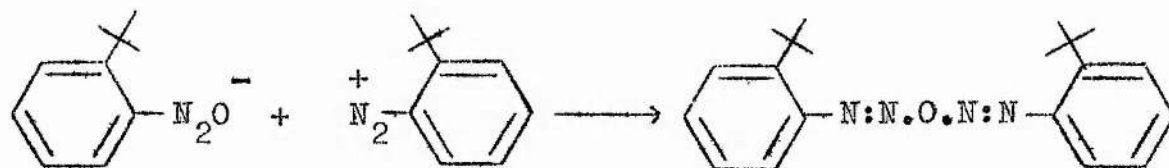
A logical extension of this argument leads to the conclusion that abstraction products should generally be formed in the reactions of acetylarylnitrosamines. Unfortunately most published reports make no reference to the presence or absence of such products.

The formation of *t*-butylbenzene (and of biphenyl) in the decompositions of the isomeric *t*-butyl-N-nitrosoacetanilides in benzene can therefore be rationalised in terms of radical abstraction, the hydrogen donor for the



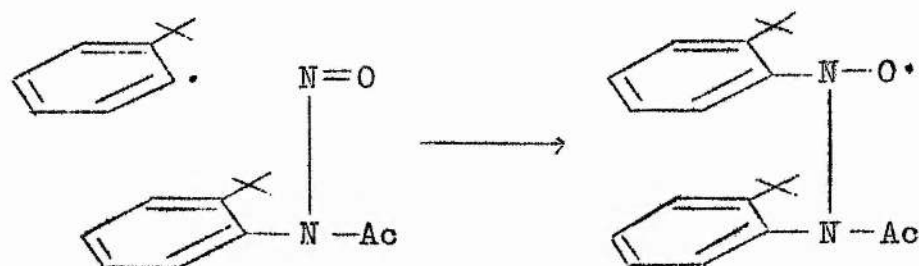
o-nitrosamido differing from that for the other isomers. As will be seen later, however, this simple explanation may not, by itself, be sufficient.

Allowing that both 2-*t*-butylbiphenyl and *t*-butylbenzene are radical products, together they account for only a fraction of the o-*t*-butyl-N-nitrosoacetanilide, suggesting that radical formation is but a minor course of decomposition. In Rüchardt and Freudenberg's scheme, as applied to the decomposition of this nitrosamido, the radical precursor would be the diazoanhydride formed by combination of an o-*t*-butylphenyl diazotate anion and an o-*t*-butylbenzenediazonium cation:



Provided the ions are formed, there is no steric reason why they should not unite, and ultimately yield the aryl radical, although the bulky substituents will certainly limit the possible configurations of the anhydride. A crucial part of the scheme proposed by Perkins and his colleagues<sup>152</sup> for the decomposition of N-nitrosoacetanilide in benzene is the formation of a chain-carrying nitroxide radical by attack of a phenyl radical on the nitrosamido. In the case of o-*t*-butyl-N-nitrosoacetanilide it can be seen from molecular models that such a reaction would be

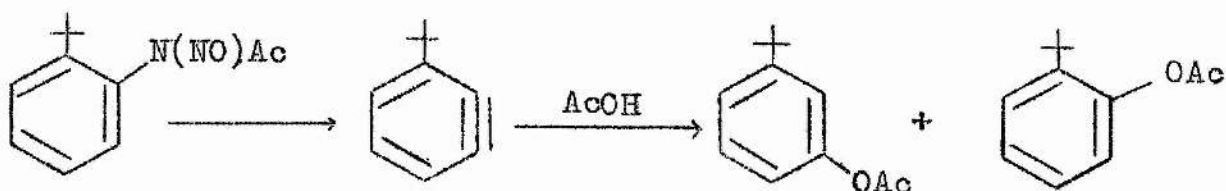
subject to severe steric hindrance:



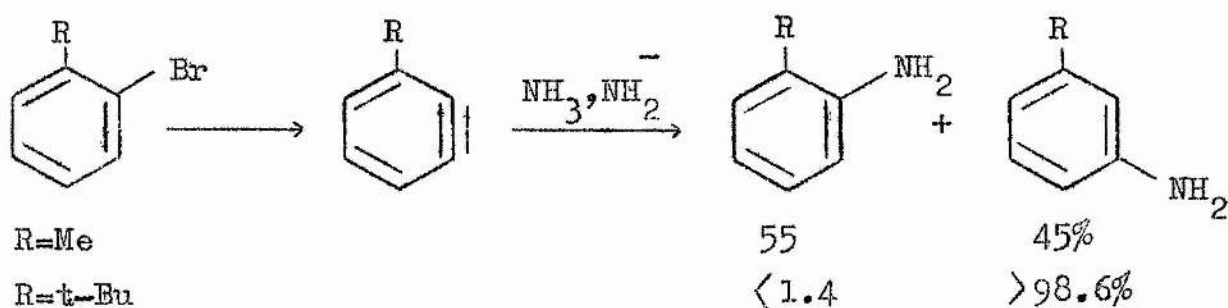
A bulky substituent in the m-position might also be expected to encumber to some extent formation of the nitroxide radical; it will be noted that the yield of 3-t-butylbiphenyl from m-t-butyl-N-nitrosoacetanilide is considerably less than that of 4-t-butylbiphenyl from the p-isomer. Attempts have been made to study the decomposition of o-t-butyl-N-nitrosoacetanilide in the cavity of an e.s.r. spectrometer.<sup>202</sup>

The signals observed have shown poor reproducibility and no definite conclusion can yet be drawn as to the presence or absence of a radical chain-carrier in this reaction.

That o-t-butyl-N-nitrosoacetanilide gave o- and m-t-butylphenyl acetates (37.8 and 17.4m/100m) but not the p-isomer was in agreement with the results of Cadogan and Hibbert,<sup>8</sup> although they obtained a rather lower total yield of ester (46m/100m). Formation of the m-acetate would seem to require a dehydroaromatic intermediate (but see "The Ersatz Aryne"<sup>203</sup>) and it might be that the o-isomer is formed in the same way:

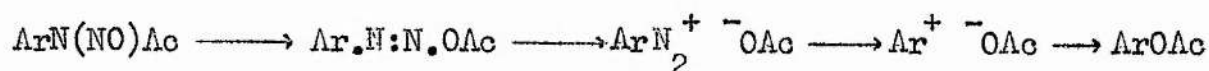


On the other hand, it could be argued that the bulky *t*-butyl group will direct attack on 3-*t*-butylbenzoyne to position one, yielding exclusively *m*-*t*-butylphenyl acetate. It was not possible to test this hypothesis directly by studying the addition of acetic acid to 3-*t*-butylbenzoyne, but the reaction of *o*-bromo-*t*-butylbenzene with sodamide in liquid ammonia was investigated. The result is shown below, together with that from other workers<sup>109</sup> for the corresponding reaction of *o*-bromotoluene:



The vast difference between the relative yields of the *o*-substituted anilines can not be attributed to differences in the electronic properties of the two alkyl groups and must therefore be a consequence of steric inhibition of attack at position two in 3-*t*-butylbenzoyne. It thus seems probable that most of the *o*-*t*-butylphenyl acetate formed by the decomposition of *o*-*t*-butyl-*N*-nitroso-

acetanilide in benzene arises by a non-aryne mechanism, and moreover, since the instability of the acetoxy radical<sup>12,13</sup> effectively precludes a homolytic pathway, the most plausible mechanism is that in which a carbonium ion is formed, possibly as part of an ion pair:



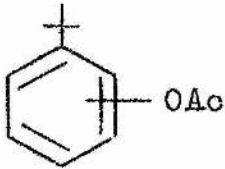
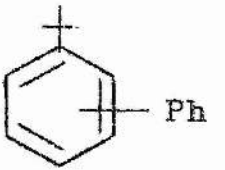
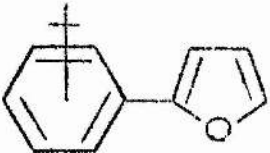
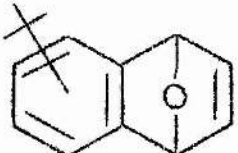
An analogous mechanism can account for the formation of m-t-butylphenyl acetate (7.9m/100m) and p-t-butylphenyl acetate (0.5m/100m) in the reactions of the m- and p-nitrosamides.

It is interesting to note that the highest ratio of ester to biaryl found by Brydon and Cadogan<sup>155</sup> in their investigation of the reactions of o-substituted acetylarlyl-nitrosamines - 0.5:1 for 2-(N-nitrosoacetamido)biphenyl - is only slightly greater than the ratio of m-t-butylphenyl acetate to 3-t-butylbiphenyl (0.4:1) formed in the decomposition of m-t-butyl-N-nitrosoacetanilide. In the latter case, however, the absence of p-t-butylphenyl acetate indicates that 4-t-butylbenzyne is not an intermediate, although participation by 3-t-butylbenzyne can not be discounted simply because no o-acetate is formed.

Reactions of t-Butyl-N-nitrosoacetanilides with Furan in Benzene.- Table 8 overleaf contains some of the information obtained from a study of the reactions of the

TABLE 8

Reactions of *t*-Butyl-N-nitrosoacetanilides with Furan in Benzene

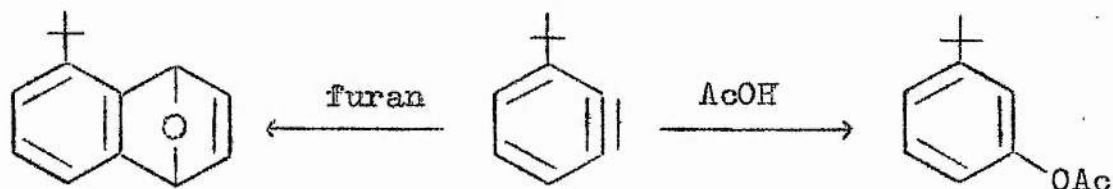
Product	Yield (m/100m nitrosamide)		
	ortho	meta	para
<i>t</i> -Butylbenzene	3.5(10.2)	8.7(4.2)	5.8(5.9)
Biphenyl	0.9(3.9)	0.3(0.3)	0.1(0.4)
 <i>o</i> -	36.9(37.8)	0 (0)	0 (0)
<i>m</i> -	0 (17.4)	9.0(7.9)	0 (0)
<i>p</i> -	0 (0)	0 (0)	0.3(0.5)
 2-	3.0(2.3)	0 (0)	0 (0)
3-	0 (0)	11.2(19.4)	0 (0)
4-	0 (0)	0 (0)	18.6(36.4)
 <i>m</i> -	- -	7.0 -	0 -
<i>p</i> -	- -	0 -	16.6 -
 5-	20.5 -	0 -	- -
6-	- -	0 -	0 -
ArNHAc	1.9(0.3)	13.1(14.2)	8.7(5.8)
Accountance (%) of Ar	65.8(68.0)	49.0(45.7)	50.0(48.6)

Figures in parenthesis are yields in pure benzene.

isomeric *t*-butyl-N-nitrosoacetanilides in benzene containing furan (2m/m nitrosamide). The yields of products from the decomposition in pure benzene are, where relevant, included for purposes of comparison.

The addition of furan had an effect on the decomposition of the m- and p-nitrosamides comparable with its influence on the reaction of unsubstituted N-nitrosoacetanilide, viz. diversion of some of the aryl radicals from attack on benzene to substitution at position two in furan. In each case the combined yield of *t*-butylbiphenyl and *t*-butylphenylfuran was similar to the yield of *t*-butylbiphenyl obtained in pure benzene. The only other change of note was an unexpected (and inexplicable) increase in the yield of *t*-butylbenzene from m-*t*-butyl-N-nitrosoacetanilide.

o-*t*-Butyl-N-nitrosoacetanilide afforded the aryne adduct, 5-*t*-butyl-1,4-dihydronaphthalene-1,4-ondoxido (20.5m/100m), to the exclusion of m-*t*-butylphenyl acetate:



In some respects these results are enigmatic. The decomposition of benzenediazonium-2-carboxylate in benzene containing benzoic acid (1.5-2.0m/m diazonium salt) is

reported to give phenyl benzoate in 22-25% yield.<sup>68</sup> Since it has also been shown that the yield of ester is only slightly dependent on the strength of the acid,<sup>68</sup> it is reasonable to suppose that phenyl acetate will be formed in similar yield from benzyne and acetic acid in benzene. The concentration of acid at any instant during the decomposition of o-t-butyl-N-nitrosoacetanilide is, of necessity, low, and it might therefore be concluded that only a small proportion of the aryne generated is accounted for by m-t-butylphenyl acetate. The yield of 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide formed in the presence of furan - an efficient aryne scavenger - is, however, only slightly greater than the yield of m-t-butylphenyl acetate produced in its absence. Further, any suggestion that the ester is formed by a cage mechanism, or in a concerted process, must be examined critically in view of the total absence of m-t-butylphenyl acetate from the products when the diene is present. The only rational explanation appears to be that a cage mechanism is operative in pure benzene, but not in the presence of the arynophile.

In contrast to the reactions of the m- and p- nitrosamides, o-t-butyl-N-nitrosoacetanilide gave a slightly increased yield of t-butylbiphenyl, and a much reduced yield of t-butylbenzene, when furan was added to the benzene solvent.



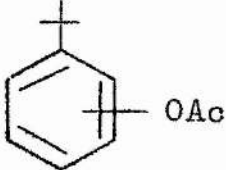
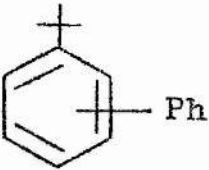
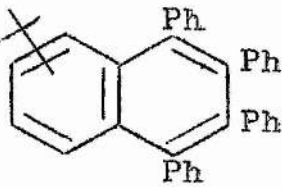
Might it be that in the absence of an aryneophile, some 3-t-butylbenzyne suffers reduction to t-butylbenzene ? The results of the decomposition of o-t-butyl-N-nitrosoacetanilide in the presence of dienes other than furan should assist in the search for an answer to this question.

Reactions of t-Butyl-N-nitrosoacetanilides in Benzene in the presence of 2,3,4,5-Tetraphenylcyclopentadienone.- On the following page, in Table 9, is a summary of the important results from the decomposition of o-, m-, and p-t-butyl-N-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone.

The reactions of m- and p-t-butyl-N-nitrosoacetanilide in the presence of 2,3,4,5-tetraphenylcyclopentadienone were marked by large decreases in the yield of t-butylbenzene and t-butylbiphenyl, while the amounts of ester were greater than those formed in pure benzene. Aryne adducts (12.1 and 12.1m/100m) were isolated from both decompositions, that formed by m-t-butyl-N-nitrosoacetanilide being a mixture of 5- and 6-t-butyl-1,2,3,4-tetraphenylnaphthalenes (3.9 and 6.3m/100m after purification). The products of the reactions of both of these nitrosamides in benzene, and in benzene containing furan, point strongly to the absence of aryne participation, and suggest that the adducts with 2,3,4,5-tetraphenylcyclopentadienone are formed by a

TABLE 9

Reactions of *t*-Butyl-N-nitrosoacetanilides with  
2,3,4,5-Tetraphenylcyclopentadienone in Benzene

Product		Yield (m/100m nitrosamide)		
		<u>ortho</u>	<u>meta</u>	<u>para</u>
<i>t</i> -Butylbenzene		3.2(10.2)	0.5(4.2)	0.3(5.9)
Biphenyl		0.2(3.9)	0.1(0.3)	0 (0.4)
	<u>o</u> -	50.5(37.8)	0 (0)	0 (0)
	<u>m</u> -	0 (17.4)	17.2(7.9)	0 (0)
	<u>p</u> -	0 (0)	0 (0)	8.7(0.5)
	2-	2.6(2.3)	0 (0)	0 (0)
	3-	0 (0)	4.6(19.4)	0 (0)
	4-	0 (0)	0 (0)	4.8(36.4)
	5-	34.2 -	3.9* -	- -
	6-	- -	6.3* -	12.1 -
ArNHAc		0.7(0.3)	17.1(14.2)	5.7(5.8)
Accountance (%) of Ar		91.2(68.0)	34.4(45.7)	31.6(48.6)

\* After purification; total crude yield, 12.1m/100m.

Figures in parenthesis are yields in pure benzene.

non-aryne mechanism, as may also be the case with N-nitrosoacetanilide and m- and p-chloro-N-nitrosoacetanilides. Such a mechanism may, in addition, be partly responsible for the formation of 5-*t*-butyl-1,2,3,4-tetraphenylnaphthalene (34.2m/100m) by o-*t*-butyl-N-nitrosoacetanilide in a yield greater than that of the adduct with furan (20.5m/100m). It is reasonable to look for a relationship between the increased yields of ester obtained in the presence of 2,3,4,5-tetraphenylcyclopentadienone and the formation of adducts; and since only one of the possible isomeric acetates is formed by both m- and p-nitrosamides, there is further reason to doubt that an aryne intermediate is responsible. The reduced yields of *t*-butylbenzene, biphenyl, and *t*-butylbiphenyl from the m- and p-nitrosamides may be simply explained by assuming that these products derive, directly or indirectly, from *t*-butylphenyl radicals, and that the radicals react very readily with 2,3,4,5-tetraphenylcyclopentadienone. Such an explanation is supported by the low yield of biphenyl (1.5m/100m) formed in the decomposition of phenylazotriphenylmethane in benzene in the presence of the diene.<sup>155</sup> Is it not possible, however, that introduction of the arynophile actually suppresses the supply of aryl radicals? A simplified form of Rüchardt and Freudenberg's scheme,<sup>125</sup> modified to include a possible heterolytic



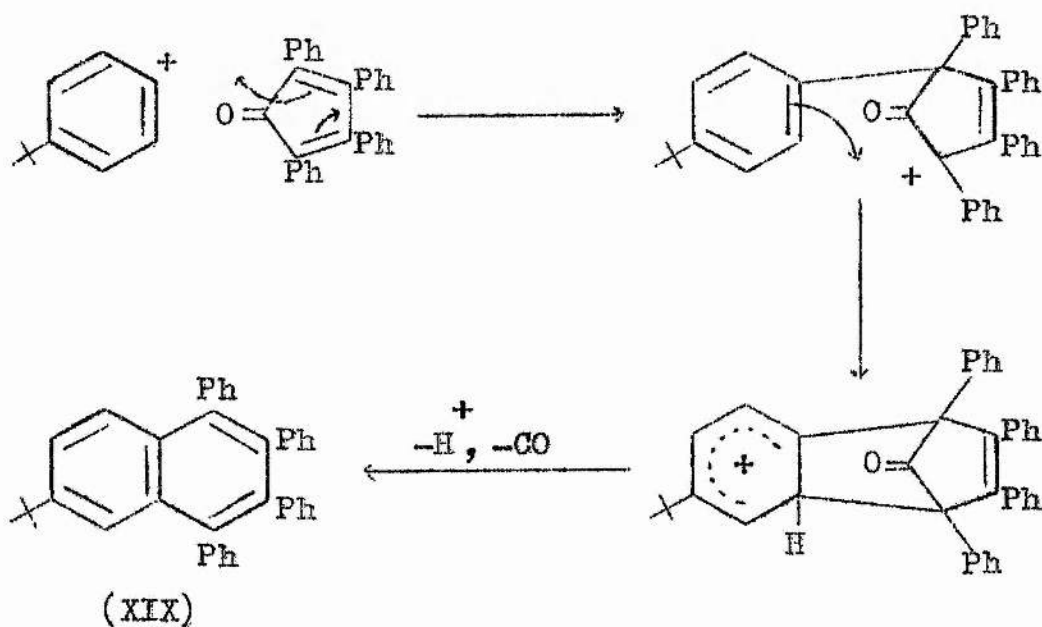
control experiment in which no radical inhibitor was present; they differ little from those obtained earlier for the decomposition of p-t-butyl-N-nitrosoacetanilide in benzene, but are included for purposes of comparison since then all three sets of results refer to the same sample of nitrosamide, and to identical reaction conditions.

<u>"Galvinoxyl" (m/100m nitrosamide)</u>	18.8	4.5	0.0
<u>Products (m/100m):</u>			
t-Butylbenzene	1.4	3.1	4.6
<u>p</u> -t-Butylphenyl acetate	1.3	1.6	1.0
4-t-Butylbiphenyl	13.1	26.3	30.4

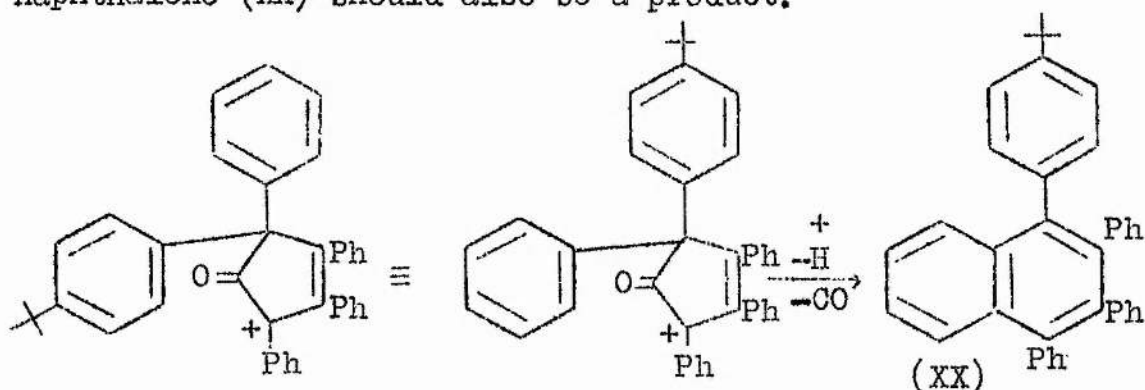
The yield of ester was increased by the presence of the radical inhibitor, but the changes were not sufficient to provide convincing confirmation of the proposed theory. The marked decreases in the yields of t-butylbiphenyl and t-butylbenzene do, however, indicate a common radical precursor for both of these products, and lend support to the suggestion of a non-radical route to the ester. It is also significant that the combined yield of biaryl and t-butylbenzene was reduced by an amount (5.6 or 20.5m/100m) greater than the initial concentration of "Galvinoxyl" (4.5 or 18.8m/100m). Even allowing for complete consumption of the inhibitor, and supposing that

every radical intercepted would otherwise have formed either *t*-butylbenzene or 4-*t*-butylbiphenyl, it is clear that each molecule of "Galvinoxyl" can account for more than one aryl radical. These observations thus provide additional confirmation of Rüchardt and Freudenberg's postulate<sup>125</sup> that the phenyl radicals from *N*-nitrosoacetanilide are formed in a chain process rather than by simple homolysis of covalent benzenediazoacetate.

It was suggested earlier that the increased yield of (for example) *p*-*t*-butylphenyl acetate from *p*-*t*-butyl-*N*-nitrosoacetanilide in the presence of 2,3,4,5-tetraphenylcyclopentadienone might be related in some way to the formation of adduct. While the ester probably results from the *p*-*t*-butylphenyl carbonium ion, is it conceivable that the adduct could also be formed from this intermediate ?



Closer examination of the above scheme illustrating how 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene (XIX) might be formed suggests that 1-(*p*-*t*-butylphenyl)-2,3,4-triphenylnaphthalene (XX) should also be a product:



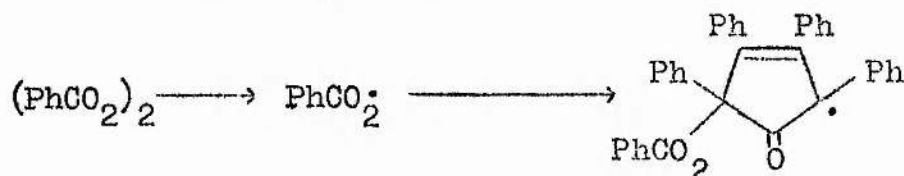
The adduct isolated from the reaction of *p*-*t*-butyl-*N*-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone had been identified as (XIX) and was subsequently shown to be identical to 6-*t*-butyl-1,2,3,4-tetraphenylnaphthalene prepared from an authentic source of 4-*t*-butylbenzyne.

2-(*p*-*t*-Butylphenyl)-3,4,5-triphenylcyclopentadienone having been synthesised, adduct (XX) was obtained from its reaction with benzyne. It was then possible to establish by i.r. spectroscopy (p. 147) that the crude adduct from the reaction of *p*-*t*-butyl-*N*-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone contained no 1-(*p*-*t*-butylphenyl)-2,3,4-triphenylnaphthalene [4.3% of (XX) in the crude adduct, corresponding to a yield of 0.55m/100m, would have been detected]. It may be concluded that an aryl carbonium ion is not responsible

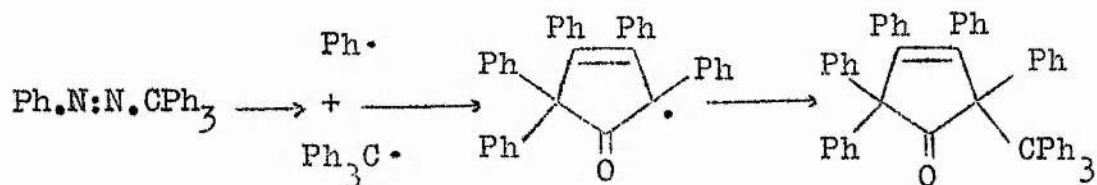


for the formation of the 2,3,4,5-tetraphenylcyclopentadienone-adduct by p-t-butyl-N-nitrosoacetanilide; and since the presence of a t-butyl group in the p-position is unlikely to have a great effect on the reaction of N-nitrosoacetanilide, this conclusion is most probably valid for the unsubstituted nitrosamide as well.

Brydon and Cadogan<sup>155</sup> found that, unlike N-nitrosoacetanilide, phenyl radical sources such as phenylazotriphenylmethane and dibenzoyl peroxide do not give 1,2,3,4-tetraphenyl-naphthalene in their reaction with 2,3,4,5-tetraphenylcyclopentadienone. At first sight these observations might appear to exclude the possibility that phenyl radicals are responsible for the formation of 1,2,3,4-tetraphenyl-naphthalene by N-nitrosoacetanilide. It is well known, however, that benzyloxy radicals can react with aromatic substrates such as naphthalene<sup>204</sup> and anthracene<sup>205</sup> more rapidly than they fragment to phenyl radicals and carbon dioxide; the possibility that phenyl radicals do not result from the decomposition of dibenzoyl peroxide in benzene containing 2,3,4,5-tetraphenylcyclopentadienone can not, therefore, be ignored, e.g.



This is not the case with phenylazotriphenylmethane, but here the resonance-stabilised triphenylmethyl radicals might conceivably cause complications, e.g.



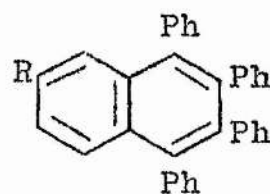
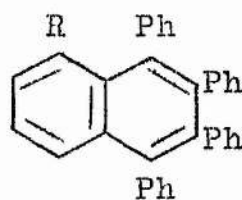
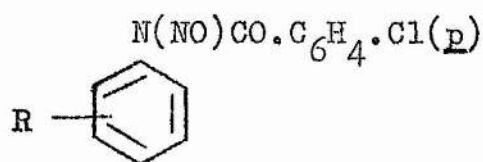
It was argued that the adduct formed by p-t-butyl-N-nitrosoacetanilide would be a mixture of isomers were an aryl carbonium ion the intermediate; equally, two products should result from an aryl-radical (or aryl-carbanion) mechanism. The absence of 1-(p-t-butylphenyl)-2,3,4-triphenylnaphthalene from the products of the reaction of p-t-butyl-N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone thus provides valuable confirmation that phenyl radicals are not responsible for the adduct formed by N-nitrosoacetanilide.

If the adduct formed by N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone does not arise through intermediacy of true benzyne, nor yet via a phenyl radical, carbanion or carbonium ion, it is probable that the reactive species still contains nitrogen. A possible intermediate is the dipolar species (XXI) formed by removal of an o-proton from the diazonium cation. In the scheme shown below, the equilibrium between the cation and its

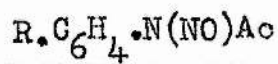


summarised below:

	<u>PhN(NO)COR</u>	<u>Solvent</u>	<u>Yield of adduct (m/100m)</u>
1.	R = Me	Benzene	25
2.	Me	CCl <sub>4</sub>	21
3.	Me	Tetrahydrofuran	23.8
4.	Me	Furan	0
5.	Me	Pyridine	0
6.	p-Cl.C <sub>6</sub> H <sub>4</sub> -	Benzene	37
7.	p-Cl.C <sub>6</sub> H <sub>4</sub> -	CCl <sub>4</sub>	37
8.	p-CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> -	CCl <sub>4</sub>	29
9.	p-NO <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> -	CCl <sub>4</sub>	14



10.	R = <u>o</u> -Br	Benzene	0	-
11.	<u>o</u> -Br	CCl <sub>4</sub>	0	-
12.	<u>m</u> -Br	Benzene	73	0
13.	<u>m</u> -Br	CCl <sub>4</sub>	70	0
14.	<u>p</u> -Br	CCl <sub>4</sub>	-	4
15.	<u>m</u> -Me	CCl <sub>4</sub>	21	12
16.	<u>p</u> -Me	CCl <sub>4</sub>	-	1
17.	<u>m</u> -NO <sub>2</sub>	CCl <sub>4</sub>	63	0
18.	<u>p</u> -NO <sub>2</sub>	CCl <sub>4</sub>	-	0



19.	R = <u>o</u> -Cl	Benzene	0	-
20.	<u>m</u> -Cl	Benzene	18.8	0
21.	<u>p</u> -Cl	Benzene	-	4.3
22.	<u>o</u> -Bu <sup>t</sup>	Benzene	34.2	-
23.	<u>m</u> -Bu <sup>t</sup>	Benzene	3.9	6.3
24.	<u>p</u> -Bu <sup>t</sup>	Benzene	-	12.1

(Experiments 19-24 are described in this thesis; the other results are due to Brydon, Cadogan and Thomson.<sup>155,156</sup>). Several points which emerge from these results merit attention:

i) A particular acylarylnitrosamine produces a similar yield of adduct in benzene and in carbon tetrachloride, suggesting a common mechanism in the two solvents (1,2; 6,7; 10,11; 12,13).

ii) The yield of 1,2,3,4-tetraphenylnaphthalene depends on the nature of the acyl group, but is not simply related to the base strength of the acylate anion (2,7,8,9).

iii) An acylarylnitrosamine with an electron attracting o-substituent in the anilino moiety does not form an adduct with 2,3,4,5-tetraphenylcyclopentadienone (10,11,19).

Since the adduct from o-t-butyl-N-nitrosoacetanilide arises, in part at least, from a true aryne, no generalisation can

be made about the effect of +I o-substituents.

iv) An acylarylnitrosamine with a p-substituent in the anilino moiety (14,16,18; 21,24) yields less adduct than the corresponding unsubstituted compound (7; 1).

v) A m-substituent in the anilino moiety exerting a -I effect (13,17,20) causes the formation of only one adduct, corresponding to the 3-substituted benzyne, in a yield greater (m-Br, m-NO<sub>2</sub>) or less (m-Cl) than the yield of adduct from the unsubstituted nitrosamide.

vi) Both of the possible adducts are formed by nitrosamides with a +I m-substituent in the anilino moiety (15,23).

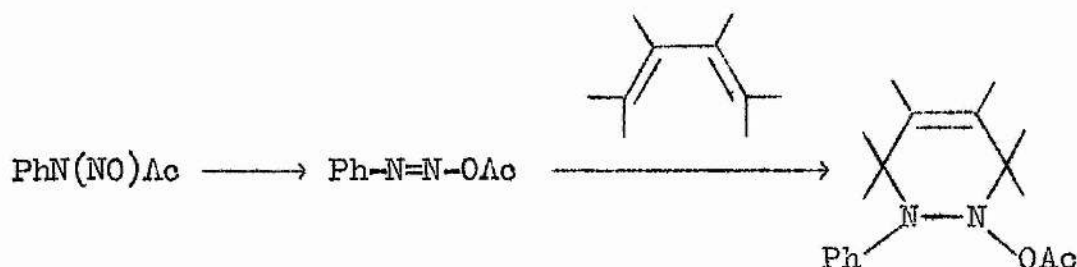
vii) 1,2,3,4-Tetraphenylnaphthalene is not formed in furan (4), where normal radical products result, or pyridine (5), where phenylpyridines are not obtained either.

viii) The presence of a trace of water causes reaction 6 to proceed as it would in the absence of the arynophile.<sup>156</sup>

The mechanism under consideration would give rise to a yield of adduct dependent on the efficiency with which the acylate (or diazotate) anion could remove a proton from the o-position in the diazonium cation, in competition with the combination of diazotate and diazonium ions. The results presented above, although limited in their scope, permit of few generalisations, and will not readily be fitted to any reaction scheme. In favour of the postulated mechanism,

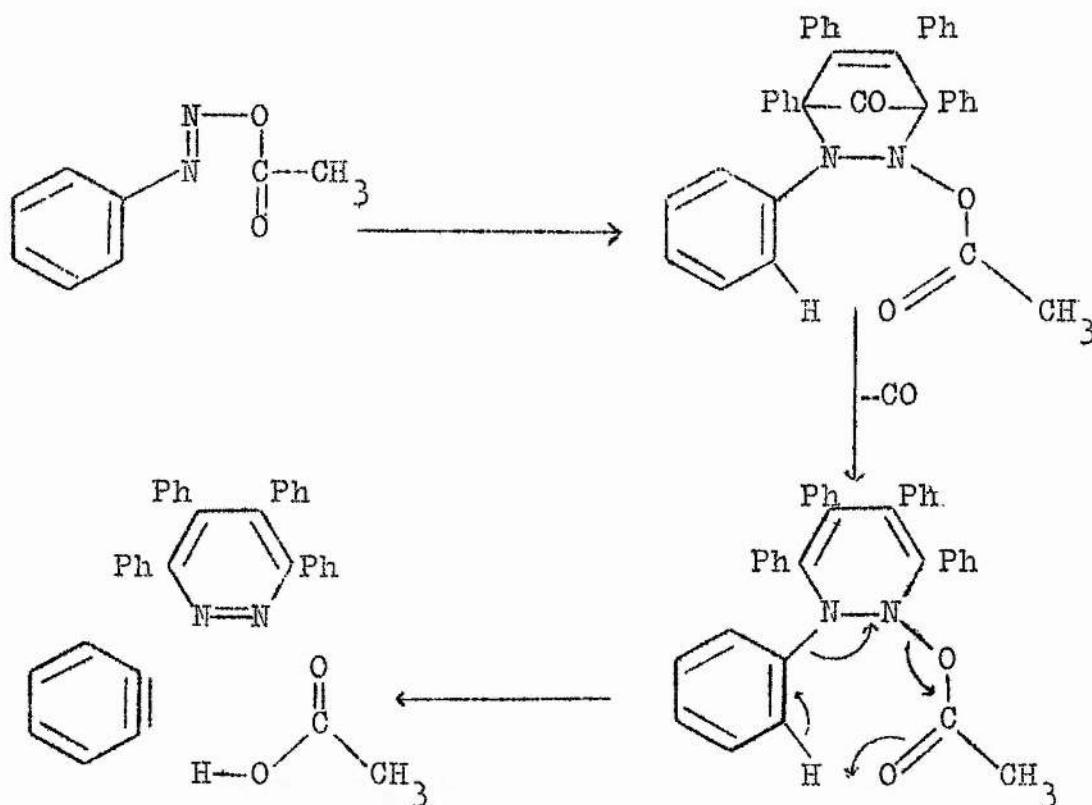
which involves the reactions of acylate, diazotate and diazonium ions, it can be said that it is not incompatible with the observed sensitivity of the yield of adduct to small changes in both the aryl and acyl groups in the acylaryl-nitrosamine. On the other hand, it has been shown that the diazonium ions in arenediazonium fluoroborates do not yield adducts with 2,3,4,5-tetraphenylcyclopentadienone when treated with such strong bases as sodium methoxide and butyllithium, although side reactions between the ketone and the base probably occur here.<sup>155</sup>

A final possibility that must at least be considered is that N-nitrosoacetanilide forms true benzyne in the presence of 2,3,4,5-tetraphenylcyclopentadienone or 1,3-diphenylisobenzofuran. The Diels-Alder addition of diethyl azodicarboxylate to dienes is well established, and several cyclic azo compounds are reported to behave similarly.<sup>206</sup> An analogous reaction might, perhaps, occur when a very reactive diene is present during the decomposition of N-nitrosoacetanilide:



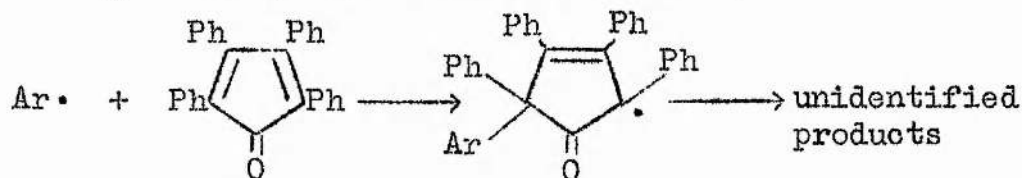


Since the benzenediazoacetate formed by rearrangement of N-nitrosoacetanilide is the trans-isomer (p.48) the addition product would probably also have the trans-configuration. While the reaction of a diene with the diazoacetate may be considered a reasonable postulate, any attempt to extend this idea to benzyne formation is, at best, speculative, e.g.



Formation of t-Butylbenzene.— Introduction of 2,3,4,5-tetraphenylcyclopentadienone to the decomposition of m- and p-t-butyl-N-nitrosoacetanilides in benzene greatly reduces the yields of t-butylbiphenyl and t-butylbenzene. If, as seems probable, this is a consequence of the diene intercepting aryl radicals (rather than preventing their

generation), it is, perhaps, surprising that the yield of 2-t-butylbiphenyl from the o-nitrosamide is not diminished by 2,3,4,5-tetraphenylcyclopentadienone. A simple explanation is to suppose that the radical-diene reaction is such as to be subject to severe steric hindrance in the case of o-t-butylphenyl radicals, for example:



Since the yield of 2-t-butylbiphenyl is not reduced by addition of the arynophile, it would be reasonable to expect that the formation of t-butylbenzene from o-t-butylphenyl radicals would not be suppressed either. The yield of t-butylbenzene (3.2m/100m) is, however, considerably lower in the presence of 2,3,4,5-tetraphenylcyclopentadienone than in its absence; and moreover, it will be recalled that a very similar result was observed for the reaction with furan in benzene. There is therefore good reason to suppose that only part (3-3.5m/100m) of the t-butylbenzene formed in the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene results from radical abstraction. How, then, is the remainder (ca. 7m/100m) formed? Since in the presence of an arynophile this part is no longer produced, the clear indication is surely that 3-t-butylbenzyne is responsible, although such a reduction of an aryne intermediate has no known

precedent. In an attempt to clarify the mechanisms by which *t*-butylbenzene is formed by *o*-*t*-butyl-*N*-nitrosoacetanilide on the one hand, and the *m*- and *p*-nitrosamides on the other, the following decompositions were examined:

- a) *o*-*t*-butyl-*N*-nitrosoacetanilide in benzene- $\text{d}_6$ ,
- b) *p*-*t*-butyl-*N*-nitrosoacetanilide in benzene- $\text{d}_6$ ,
- c) *o*-*t*-butyl-*N*-nitroso-2,2,2-trideuterioacetanilide in benzene,
- d) *p*-*t*-butyl-*N*-nitroso-2,2,2-trideuterioacetanilide in benzene.

The yield of *t*-butylbenzene was in no case significantly different from that obtained in the corresponding experiment without deuterium labelling. Mass spectroscopic examination of the *t*-butylbenzene, comparing the abundancies of the ions with  $m/e$  134, 135 etc. indicated the following compositions:

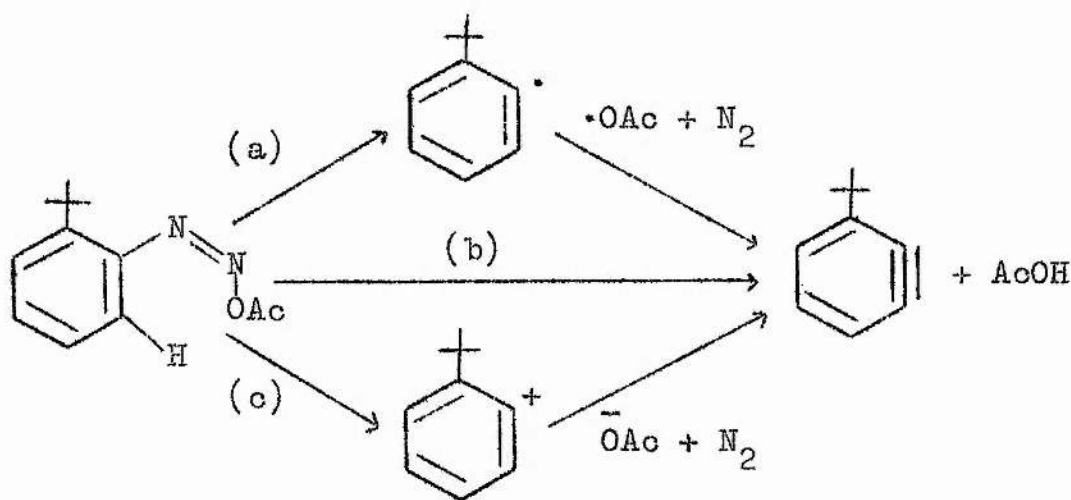
<u>Percent by weight of</u>	<u><math>\text{C}_{10}\text{H}_{14}</math></u>	<u><math>\text{C}_{10}\text{H}_{13}\text{D}</math></u>	<u><math>\text{C}_{10}\text{H}_{12}\text{D}_2</math></u>
Reaction a)	95.4	4.5	0.1
b)	69.0	30.7	0.3
c)	92.6	7.3	0.1
d)	97.9	2.1	0.0

When the calculations were repeated on the ions with  $m/e$  119, 120, etc., corresponding to the loss of a methyl group from the *t*-butyl group, the similarity of the results indicated that significant incorporation of deuterium had been restricted to the aromatic nucleus.

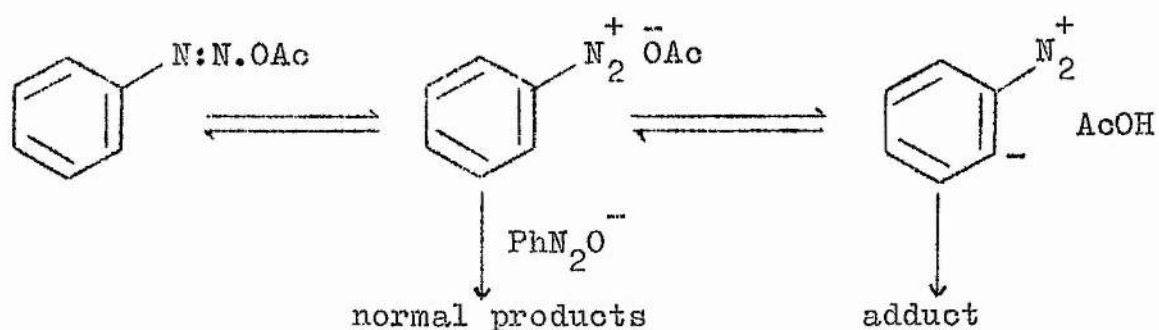
The immediate conclusion to be drawn from these results is that most of the *t*-butylbenzene formed from either *o*- or *p*-*t*-butyl-N-nitrosoacetanilide contains hydrogen derived neither from the solvent nor from the acyl group in either the nitrosamide or its decomposition products. The source of hydrogen must, in that case, be the *t*-butyl group or the aromatic nucleus of the nitrosamide, or products derived therefrom. An alternative explanation is that deuterium has been replaced by protium during the isolation of *t*-butylbenzene. It should, however, be noted that neither mineral acid nor strong base were ever present; that acetic acid was neutralised before distillation of the reaction mixture; that the temperature during distillation and preparative g.l.c. never exceeded 160°; and that g.l.c. made use of glass columns with on-column injection of the sample. Extensive isotope-exchange would not be expected to occur under such conditions. Even less probable is that replacement of protium by deuterium could cause a major change in the mechanism of formation of *t*-butylbenzene without having an appreciable effect on its yield. Thus the possibility that (for example) benzene acts as a reducing agent but benzene-d<sub>6</sub> does not, requires no further consideration. The extraordinary

results of these experiments must be viewed with suspicion until extensive control-experiments confirm or deny their validity.

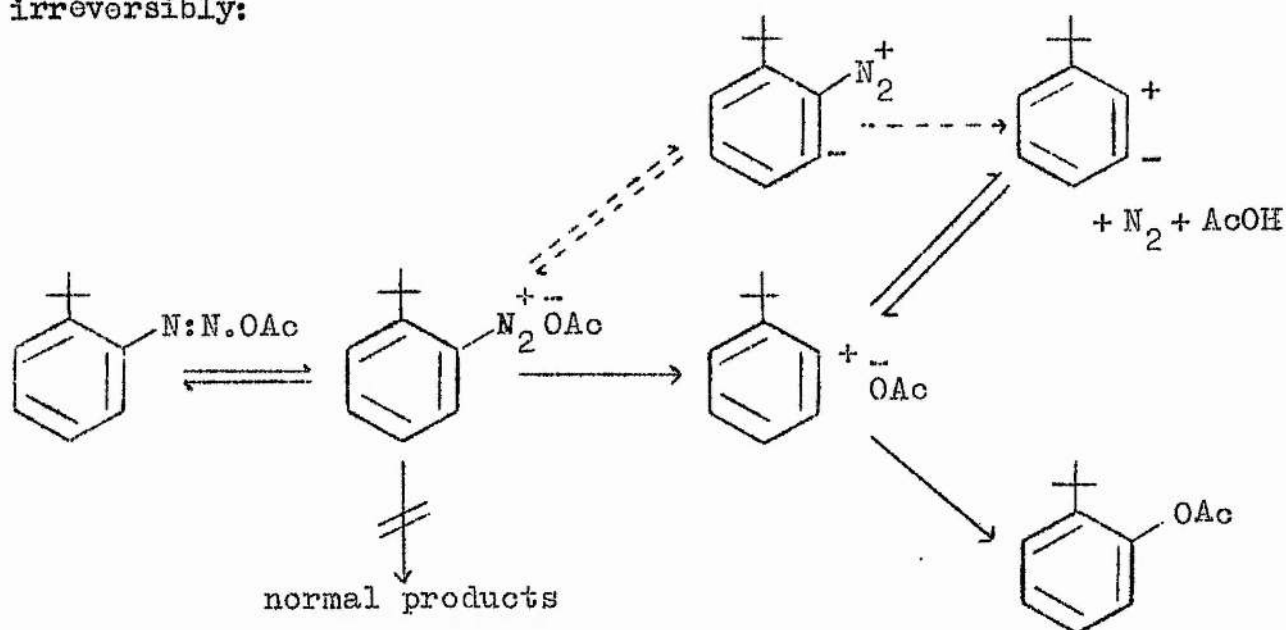
Mechanism of Decomposition of o-t-Butyl-N-nitrosoacetanilide.— Cadogan and Hibbert<sup>8</sup> suggested that the anomalous behaviour of o-t-butyl-N-nitrosoacetanilide was a consequence of the bulky o-substituent causing the nitrosamide to rearrange to the cis- (rather than the usual trans-) diazoacetate. Three possible routes to 3-t-butylbenzyne were suggested:



Of these path (a), involving unstable acetoxyl radicals, is the least probable. The results of these new investigations do not greatly assist a choice between the other possibilities, although path (c) can be readily accommodated in one of the schemes already considered to account for the formation of an adduct by N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone, i.e.



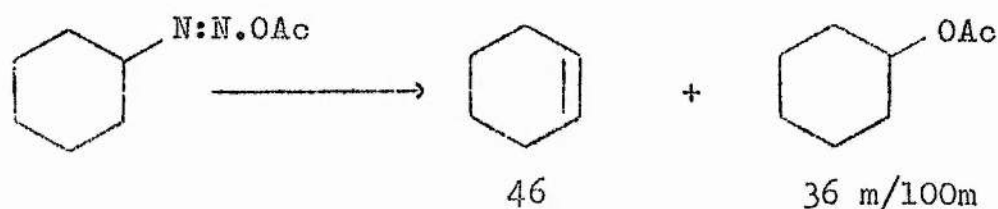
The o-t-butylbenzenediazonium cation (or its conjugate base) will undoubtedly be subject to considerable steric strain, and might consequently eliminate nitrogen rapidly and irreversibly:



o-t-Butylphenyl carbonium ions would be formed in the major reaction path, and their subsequent reaction with acetate ions (possibly as ion pairs) could result in o-t-butylphenyl acetate or 3-t-butylbenzyne. Steric inhibition of the combination of the ions might make the alternative proton-transfer reaction a more favoured

process than would otherwise be the case.

In conclusion, brief reference must be made to the remarkable (formal) similarity between the decomposition of o-t-butyl-N-nitrosoacetanilide, giving o-t-butylphenyl acetate and 3-t-butylbenzyne, and the decomposition of acylalkyl-nitrosamines such as N-cyclohexyl-N-nitrosoacetamide having a secondary alkyl group, e.g.<sup>207</sup>



It is interesting to speculate as to the possibility of the presence of a bulky substituent in the o-position causing N-nitrosoacetanilide to behave, in part at least, like an acylalkylnitrosamine.

#### 2,5-Di-t-butyl-N-nitrosoacetanilide

The behaviour of 2,5-di-t-butyl-N-nitrosoacetanilide, which contains a t-butyl group ortho to the nitrosamide function, might be expected to resemble that of o-t-butyl-N-nitrosoacetanilide. Moreover, in view of the appreciable amount of ester afforded by m-t-butyl-N-nitrosoacetanilide, it would not be surprising if here, where there is also a t-butyl substituent meta to the N-nitrosoacetamido group, a very high yield of 2,5-di-t-butylphenyl acetate were



to be formed.

The principal results from an investigation of the decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide in benzene, in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone (t.p.c.p.), in benzene containing anthracene, and in furan, are reproduced in Table 10 on the following page.

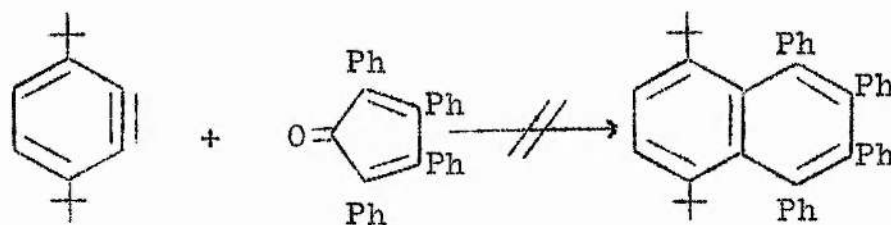
The absence of 2,5-di-*t*-butylbiphenyl from the products of decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide in benzene, together with the formation of ester in high yield, suggests that the anomalous behaviour of o-*t*-butyl-N-nitrosoacetanilide is accentuated by introduction of a second *t*-butyl group to position five. p-Di-*t*-butylbenzene and a small amount of biphenyl are therefore to be expected among the products. Since acetic acid can give only one isomer by addition to symmetrical 3,6-di-*t*-butylbenzyne, there can be no indication of the extent of aryne participation in the absence of an arynophile.

Introduction of 2,3,4,5-tetraphenylcyclopentadienone to the system had an appreciable effect only on the yield of biphenyl, which was, predictably, reduced. The absence of 5,8-di-*t*-butyl-1,2,3,4-tetraphenylnaphthalene might indicate either that 3,6-di-*t*-butylbenzyne was not formed, or that, having been formed, steric hindrance prevented

TABLE 10Reactions of 2,5-Di-t-butyl-N-nitrosoacetanilide

Product	Yield (m/100m nitrosamide)			
	Benzene	Benzene + t.p.c.p.	Benzene + C <sub>14</sub> H <sub>10</sub>	Furan
p-Di-t-butylbenzene	7.8	8.4	5.1	4.1
Biphenyl	1.3	0	0	-
2,5-Di-t-butylphenyl acetate	79.0	76.9	53.1	63.1
2,5-Di-t-butylbiphenyl	0	0	0	-
1,4-Di-t-butyltritycene	-	-	15.8	-
2,5-Di-t-butylacetanilide	0	0	0	0
2,5-Di-t-butyl-1,4-dihydronaphthalene-1,4-endoxide			-	29.7
Accountance (%) of				
Ar in ArN(NO)Ac	86.8	85.3	74.0	96.9

its reaction with the diene. Molecular models demonstrate the severe steric strain that would be present in the adduct.

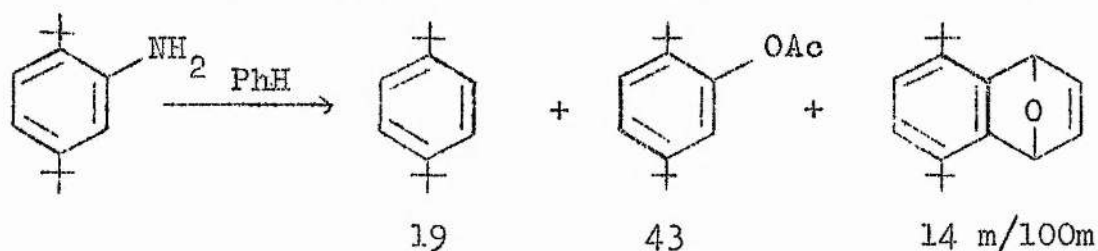


1,4-Di-*t*-butyltritycene (15.8m/100m) was isolated from the reaction of the nitrosamide with anthracene in benzene, in a yield considerably greater than that of the adduct obtained by Cadogan and Hibbert<sup>8</sup> from the corresponding reaction of *o*-*t*-butyl-*N*-nitrosoacetanilide. In common with that reaction, however, the yield of ester was reduced by more than the amount of adduct formed, while the quantity of anthracene consumed (30.3m/100m nitrosamide) further suggests that it does more than act merely as an aryneophile. The yield of *p*-di-*t*-butylbenzene (5.1m/100m) was lower in the presence of the diene than in pure benzene, indicating, perhaps, that some *p*-di-*t*-butylbenzene can be formed through an aryne intermediate.

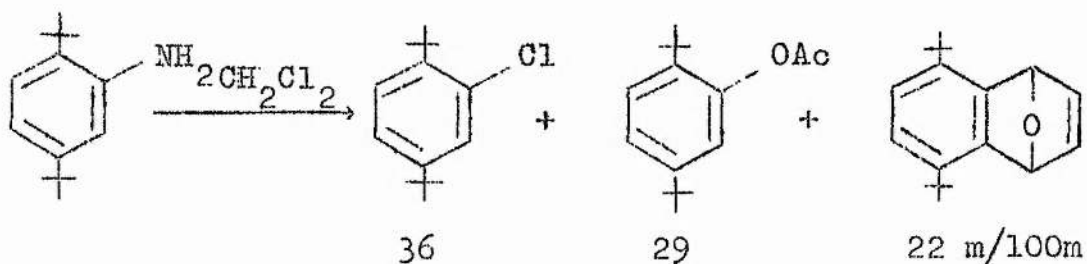
In the last reaction, where furan acts both as diene and as solvent, the yield of 5,8-di-*t*-butyl-1,4-dihydro-naphthalene-1,4-endoxide (29.7m/100m) is probably a reasonable measure of the extent of aryne participation in the decomposition of 2,5-di-*t*-butyl-*N*-nitrosoacetanilide. Equally, the yield of *p*-di-*t*-butylbenzene might conceivably

indicate the proportion of the reduction product formed in benzene via a non-aryne mechanism; although the unexpectedly high yield of 2,5-di-*t*-butylphenyl acetate (63.1m/100m; only 15.9m/100m less than in benzene) may reflect a marginal change of mechanism on passing from benzene to a solvent of higher dielectric constant.

While this work was in progress, remarkably similar results were reported by Franck and Yanagi<sup>208</sup> for the diazotisation of 2,5-di-*t*-butylaniline (with butyl nitrite) in benzene containing furan and acetic acid (1 equivalent):

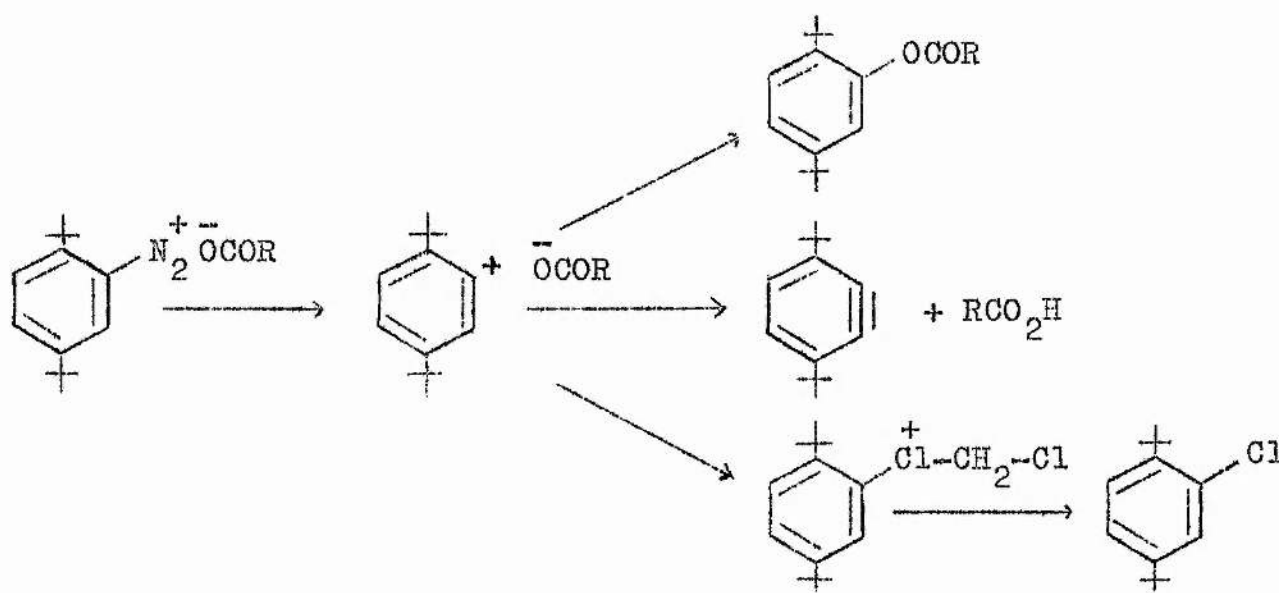


With dichloromethane as solvent the major product was 2,5-di-*t*-butylchlorobenzene:



Replacement of acetic acid by 2,2-dimethylpropanoic acid in the latter reaction resulted in a higher ratio of adduct to ester (41:19m/100m), while with this acid in dichloromethane in the absence of furan, *p*-di-*t*-butylbenzene

(28m/100m) was an important product. Franck and Yanagi<sup>208</sup> concluded that the unusual behaviour of 2,5-di-*t*-butylaniline was a consequence of the presence of a bulky *o*-substituent causing rapid elimination of nitrogen from the diazonium cation, but they did not discount the possibility of a homolytic pathway to the aryl chloride.



The ester isolated from an experiment with amine- $\text{ND}_2$  and  $\text{AcOD}$  in the presence of furan contained very little deuterium, consistent with the observation made earlier that acetic acid (or  $\text{AcOD}$ ) competes unfavourably with furan for a dehydroaromatic intermediate.

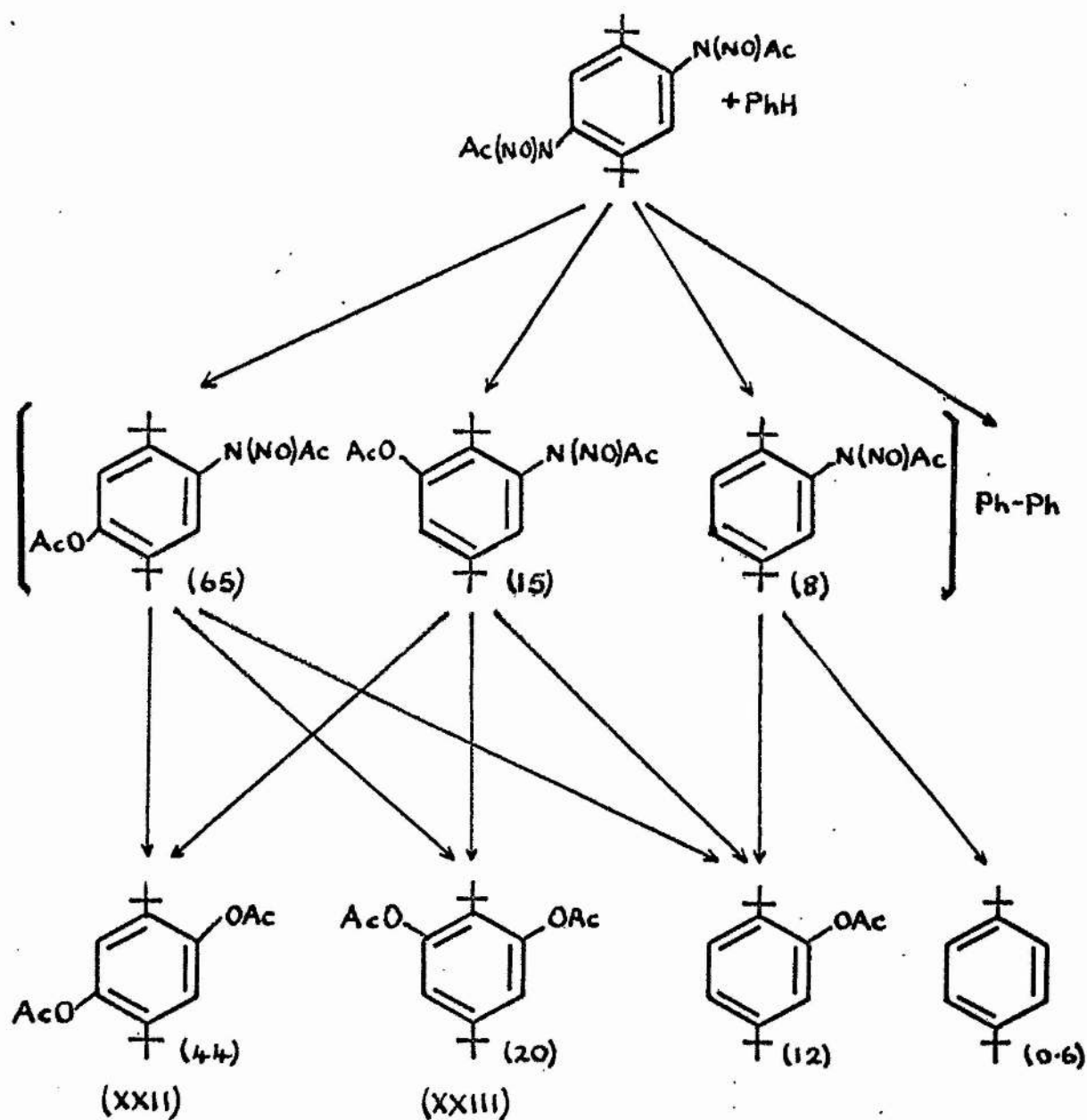
#### 1,4-Di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene

Convincing evidence of aryne participation in the decomposition of 2,5-di-*t*-butyl-*N*-nitrosoacetanilide,

together with the high accountancy of starting material as identified products, encouraged an investigation of the reactions of 1,4-di-*t*-butyl-2,5-di-(N-nitrosoacetamido)-benzene, in which the two nitrosamide functions both have an adjacent *t*-butyl substituent. The rate determining step in the decomposition of N-nitrosoacetanilide is rearrangement of the nitrosamide to benzenediazoacetate.<sup>135</sup> Although no information on the kinetics of subsequent processes was available, it seemed probable that the major course of decomposition of the dinitrosamide would be that in which complete reaction of one N-nitrosoacetamido substituent, giving products containing a single nitroso group, were followed by reaction of the second group. Support for the idea of (largely) independent reaction of the nitrosamide groups in a dinitrosamide was drawn from the observation that *p*-terphenyl results in high yield from the decomposition of *p*-di-(N-nitrosoacetamido)benzene in benzene.<sup>209</sup> Extrapolation of the results from experiments with 2,5-di-*t*-butyl-N-nitrosoacetanilide suggested that the major product from the decomposition of 1,4-di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene in benzene would be 2,5-di-*t*-butylhydroquinone diacetate (XXII), formed in part via an aryne. Significant yields of 2,5-di-*t*-butyl-

# Scheme 1

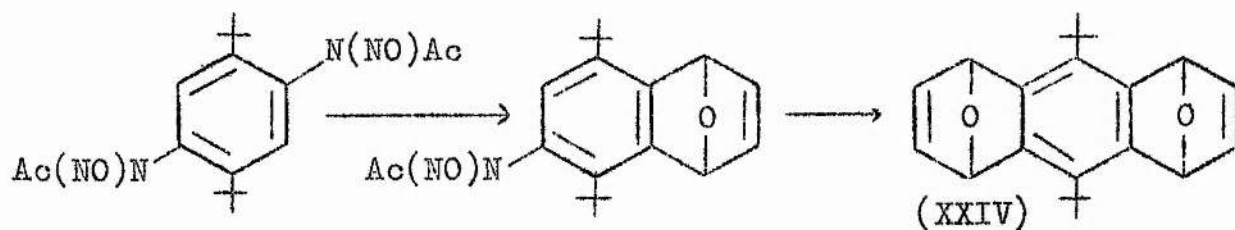
Predicted Products (and yields) of the Decomposition of  
1,4-Di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene in Benzene





resorcinol diacetate (XXIII) and 2,5-di-*t*-butylphenyl acetate were expected, together with small amounts of *p*-di-*t*-butylbenzene and biphenyl. Scheme 1 illustrates these products, their predicted yields (m/100m), shown in parentheses, being calculated on the assumption that both N-nitrosoacetamido groups behave as in 2,5-di-*t*-butyl-N-nitrosoacetanilide, and that acetic acid adds equally in both directions to an unsymmetrical aryne.

Independent reaction of the nitrosamide functions should, in the presence of an arynophile such as furan, lead to products derived formally from 1,4-di-*t*-butyldihydrobenzene, e.g.



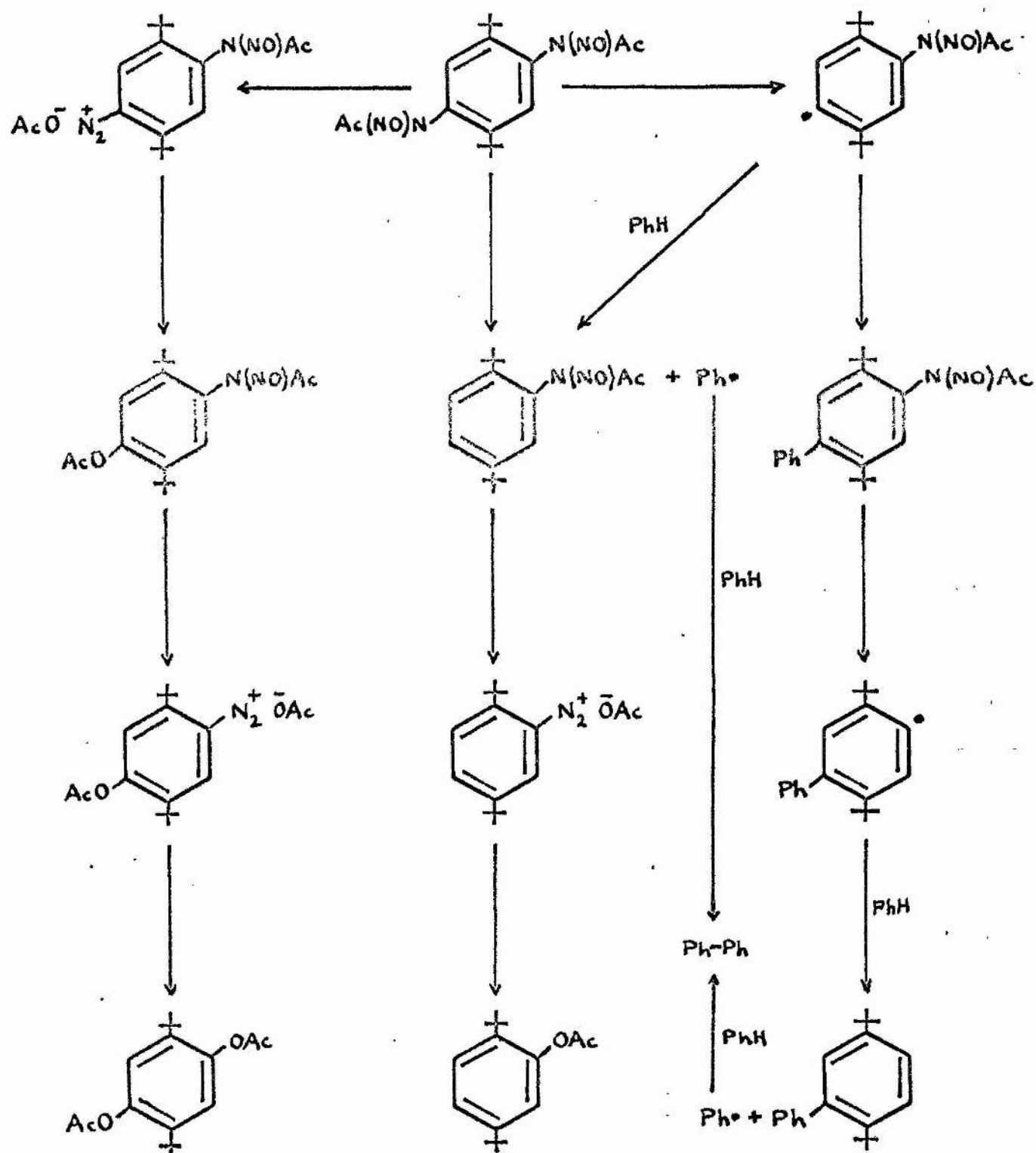
Of greater interest, however, would be the consequences of either simultaneous, or consecutive but interdependent, reaction of the two N-nitrosoacetamido substituents.

The more important products detected in the reactions of 1,4-di-*t*-butyl-2,5-di-(N-nitrosoacetamido)benzene in benzene, in benzene containing anthracene, in furan, and in trans-1,2-dichloroethylene are included in Table 11 overleaf.

TABLE 11Reactions of 1,4-Di-t-butyl-2,5-di-(N-nitrosoacetamido)benzene

Product	Yield (m/100m) dinitrosamide			
	PhH	PhH + $C_{14}H_{10}$	Furan	trans- $C_2H_2Cl_2$
p-Di-t-butylbenzene	0	0	0	0
Biphenyl	1.2	0	—	—
2,5-Di-t-butylphenyl acetate	1.6	1.2	2.7	2.6
2,5-Di-t-butylhydroquinone diacetate	15.5	12.9	8.5	15.2
2,5-Di-t-butylresorcinol diacetate	0	0	0	0
2,5-Di-t-butylbiphenyl	1.7	1.0	—	—
2,5-Di-t-butylphenol	0.25	0	1.3	0
4-Chloro-2,5-di-t-butylphenyl acetate	—	—	—	6.8
Accountance (%) of the aryl moiety in the dinitrosamide	19.05	15.1	12.5	24.6

Scheme 2

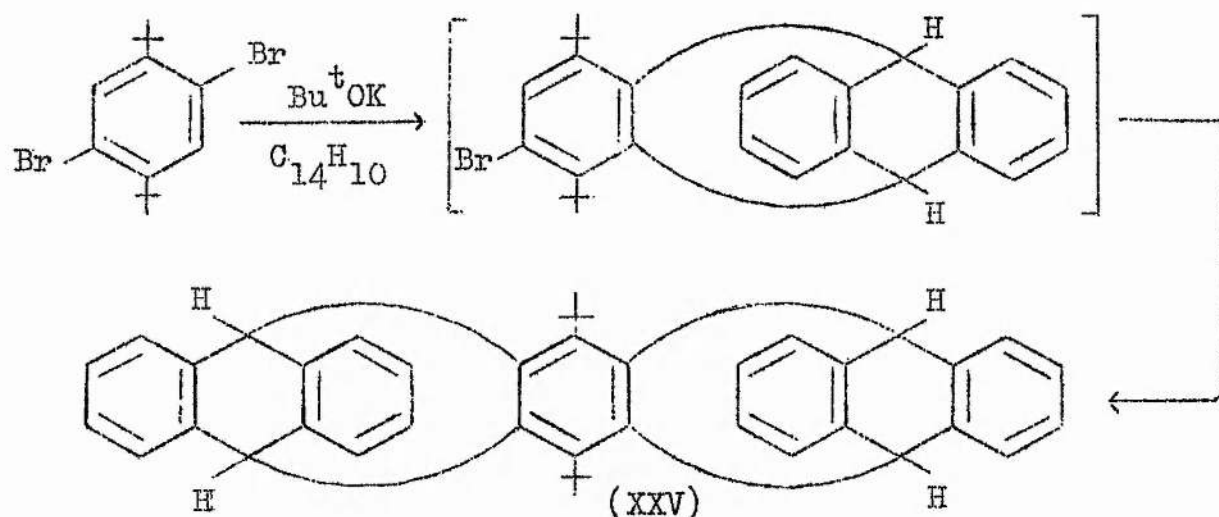


The outstanding feature common to all the reactions is the low accountancy (less than 25%) of the aryl moiety in the dinitrosamide by identifiable products. 2,5-Di-*t*-butylhydroquinone diacetate was, as predicted, the major product, but its low yield, together with the total absence of *p*-di-*t*-butylbenzene and 2,5-di-*t*-butylresorcinol diacetate, clearly indicates that the two nitrosamide functions do not react independently.

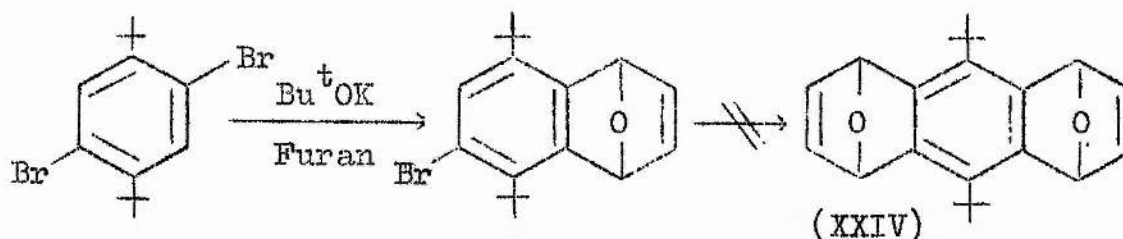
Mechanisms involving radicals and ions can, as shown in Scheme 2, account for the observed products of decomposition of the dinitrosamide in benzene, without recourse to aryne intermediates. (Only when the reactions, discussed later, of 4-acetoxy-2,5-di-*t*-butyl-N-nitrosoacetanilide were studied did the significance of a small amount of 2,5-di-*t*-butylphenol become apparent). It is surprising that 2,5-di-*t*-butylbiphenyl (1.7m/100m), not formed by the decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide in benzene, should have been detected among the products. The suggested paths to this biaryl and to 2,5-di-*t*-butylphenyl acetate require abstraction of hydrogen from the solvent by aryl radicals; biphenyl (1.2m/100m), formed from the resulting phenyl radicals, was detected.

The only notable consequence of introducing anthracene to the system was the elimination of biphenyl from the

products; and since fused polycyclic aromatic hydrocarbons are generally very reactive substrates in homolytic reactions,<sup>127</sup> this result was not unexpected. An authentic specimen of 6,13-di-*t*-butyl-5,7,12,14-tetrahydro-5,14:7,12-di-*o*-benzenopentacene (XXV) was prepared, but this adduct could not be detected among the products of the reaction of the dinitrosamide with anthracene.



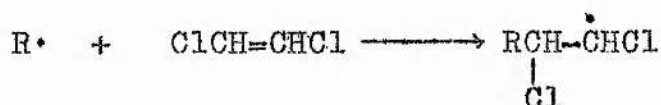
The yield of 2,5-di-*t*-butylhydroquinone diacetate (8.5m/100m) from the decomposition of the dinitrosamide in furan was approximately one half of the yield in benzene, inviting speculation that in the absence of the diene, some ester had been formed by way of an aryne. 1,4,6,9-Tetrahydroanthracene-1,4:6,9-diendoxide (XXIV) was not, however, isolated; although lacking an authentic specimen (whose attempted preparation, illustrated below, had been unsuccessful) it was not possible to prove the absence of adduct (XXIV).



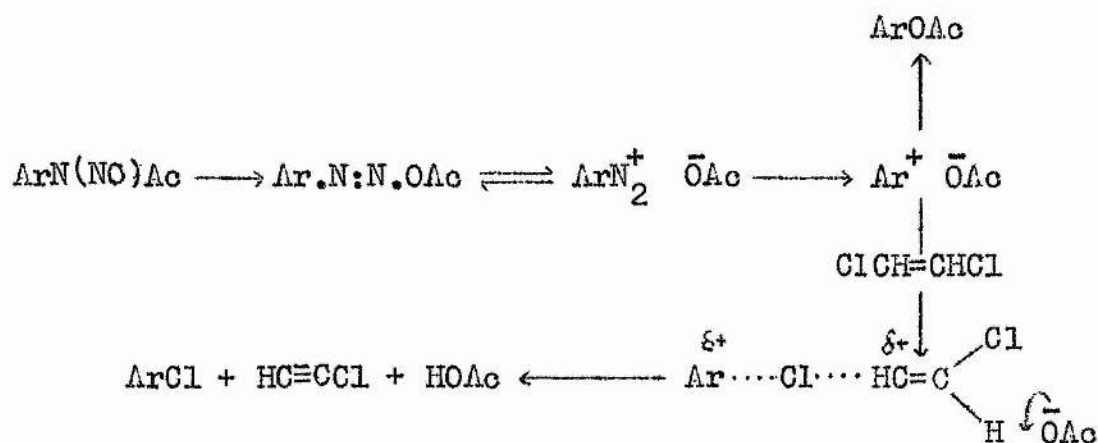
5,8-Di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide, which would arise from one nitrosamide function forming an aryne and the other being replaced by hydrogen, was not a product (0.2m/100m would have been detected).

With the expected products being formed in low yield or not at all, the question arose how, and through what intermediates, the decomposition of 1,4-di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)-benzene does proceed. In an attempt to detect any unusual intermediates that might be formed, the dinitrosamide was allowed to decompose in trans-1,2-dichloroethylene. The yields of 2,5-di-*t*-butylhydroquinone diacetate and 2,5-di-*t*-butylphenyl acetate were little different from those in benzene, and the only isolated product into which (part of) the alkene was unquestionably incorporated was 4-chloro-2,5-di-*t*-butylphenyl acetate (6.8m/100m), although it may well have provided the hydrogen necessary for the formation of 2,5-di-*t*-butylphenyl acetate. The strength of the C-Cl bond in vinyl chloride is 104 kcal. per mole,<sup>210</sup> and although no information is available, it is reasonable to expect a similar value

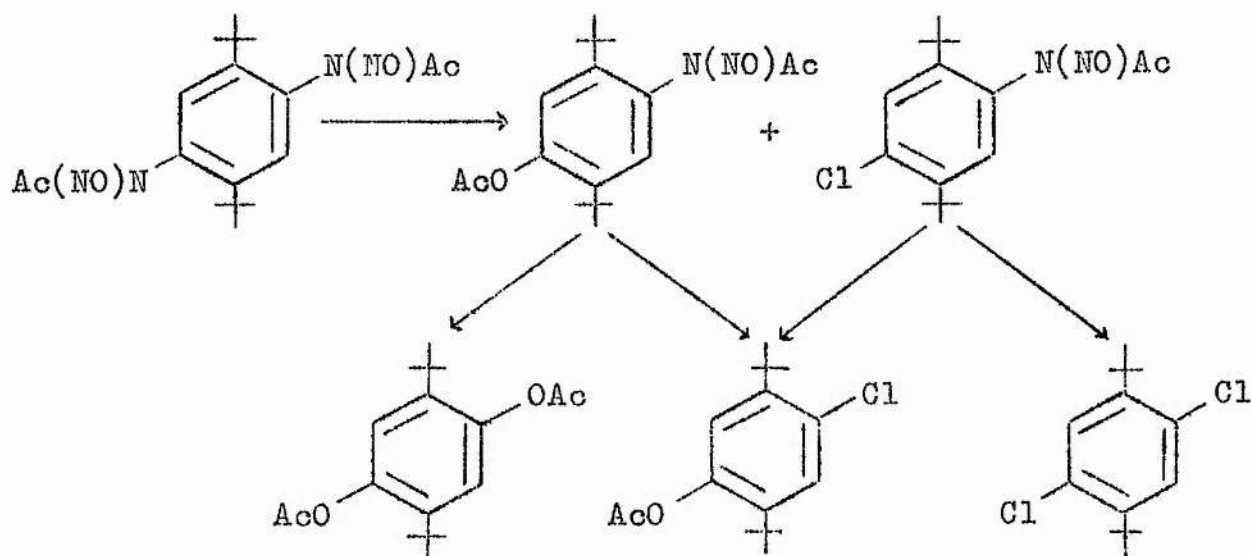
for 1,2-dichloroethylene. Lacking evidence to the contrary, it may be assumed that in general a free radical will add to the double bond:



Can radical abstraction then be ruled out as a route to 4-chloro-2,5-di-*t*-butylphenyl acetate? An argument similar to that above leads to the conclusion, confirmed experimentally, that radicals will initially add to, rather than abstract from, benzene; yet evidence for abstraction of hydrogen by *o*-*t*-butylphenyl radicals has already been presented. While radical abstraction must be regarded as a possibility, it seems more likely that the carbonium-ion mechanism leading to 2,5-di-*t*-butylhydroquinone diacetate also produces 4-chloro-2,5-di-*t*-butylphenyl acetate:







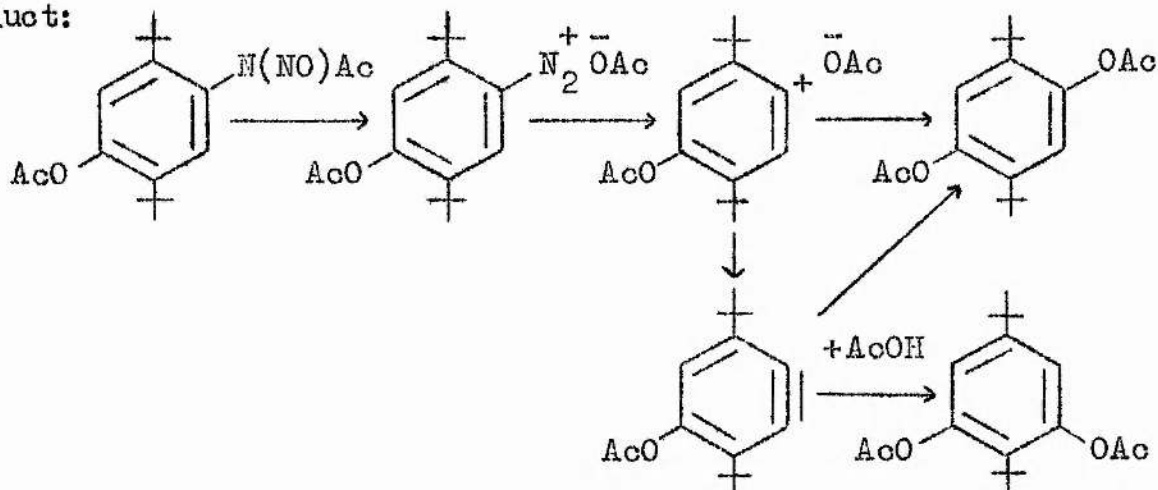
Although chloroacetylene and 1,4-di-t-butyl-2,5-dichlorobenzene were not isolated, neither was their absence from the reaction products established.

Two assumptions had been made in (incorrectly) predicting the products of decomposition of 1,4-di-t-butyl-2,5-di-(N-nitrosoacetamido)benzene in benzene: that the dinitrosamide would initially form 4-acetoxy-2,5-di-t-butyl-N-nitrosoacetanilide in high yield, and that this compound would then behave in a manner similar to 2,5-di-t-butyl-N-nitrosoacetanilide. Although the first assumption could not readily be tested, it was possible to investigate the second.

4-Acetoxy-2,5-di-t-butyl-N-nitrosoacetanilide and p-Acetoxy-N-nitrosoacetanilide

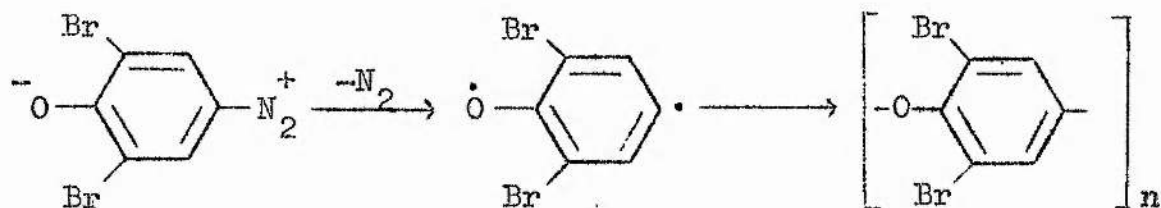
There seemed little reason to doubt that the

decomposition of 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide in benzene would produce a high yield of 2,5-di-*t*-butylhydroquinone diacetate, and since an aryne would probably participate, 2,5-di-*t*-butylresorcinol diacetate was also an expected product:



Initial examination of the reaction mixture suggested that no single product accounted for more than 6% of the nitrosamide, the major product being the totally unexpected 2,5-di-*t*-butyl-*p*-benzoquinone (5.8m/100m). 2,5-Di-*t*-butylphenol (5.1m/100m) was formed, together with small amounts of 2,5-di-*t*-butylhydroquinone diacetate, 2,5-di-*t*-butylphenyl acetate and biphenyl (2.2-2.7m/100m), but 2,5-di-*t*-butylresorcinol diacetate could not be detected. It was easily shown that under the reaction conditions the phenol could not possibly have resulted from hydrolysis of 2,5-di-*t*-butylphenyl acetate. Thus the decomposition of 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide bears little resemblance to that of 2,5-di-*t*-butyl-*N*-nitrosoacetanilide, the acetoxy group

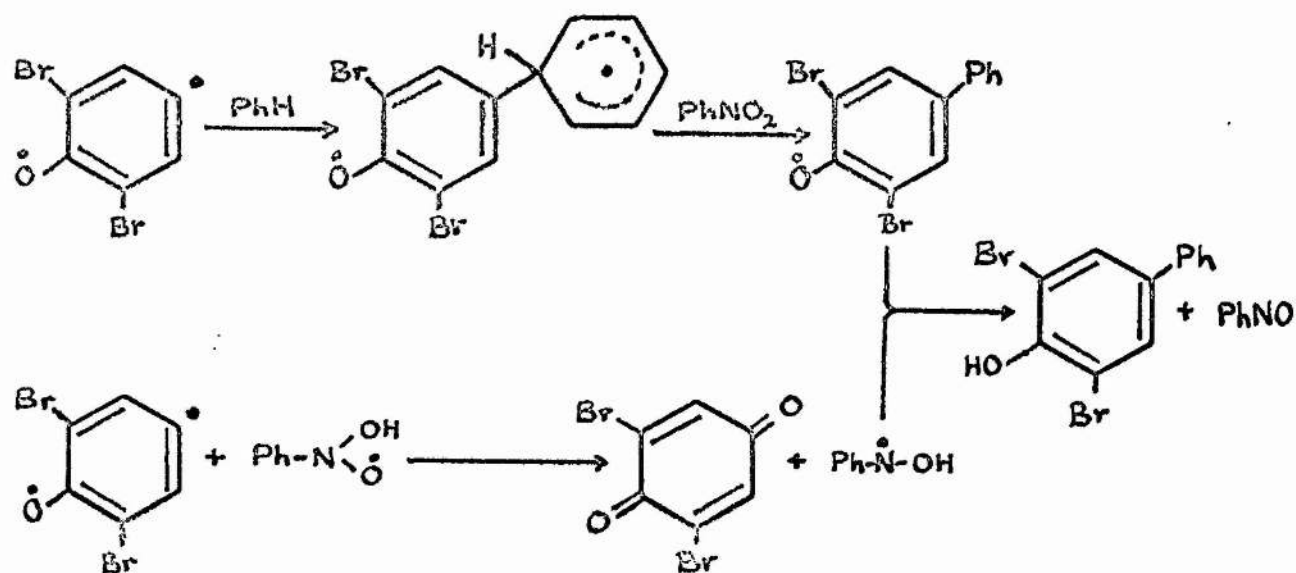
in position four exerting a marked influence on the reaction of the nitrosamide function. Before considering a possible mechanism for this reaction, attention should be given to Dewar and James' investigation<sup>211</sup> of the formation of polymers by thermal decomposition of arene-1,4-diazo-oxides. To minimise side reactions they investigated compounds such as 3,5-dibromobenzene-1,4-diazo-oxide, in which the reactive positions ortho to oxygen were blocked. They deduced that in aprotic solvents the first step was elimination of nitrogen with formation of a diradical:



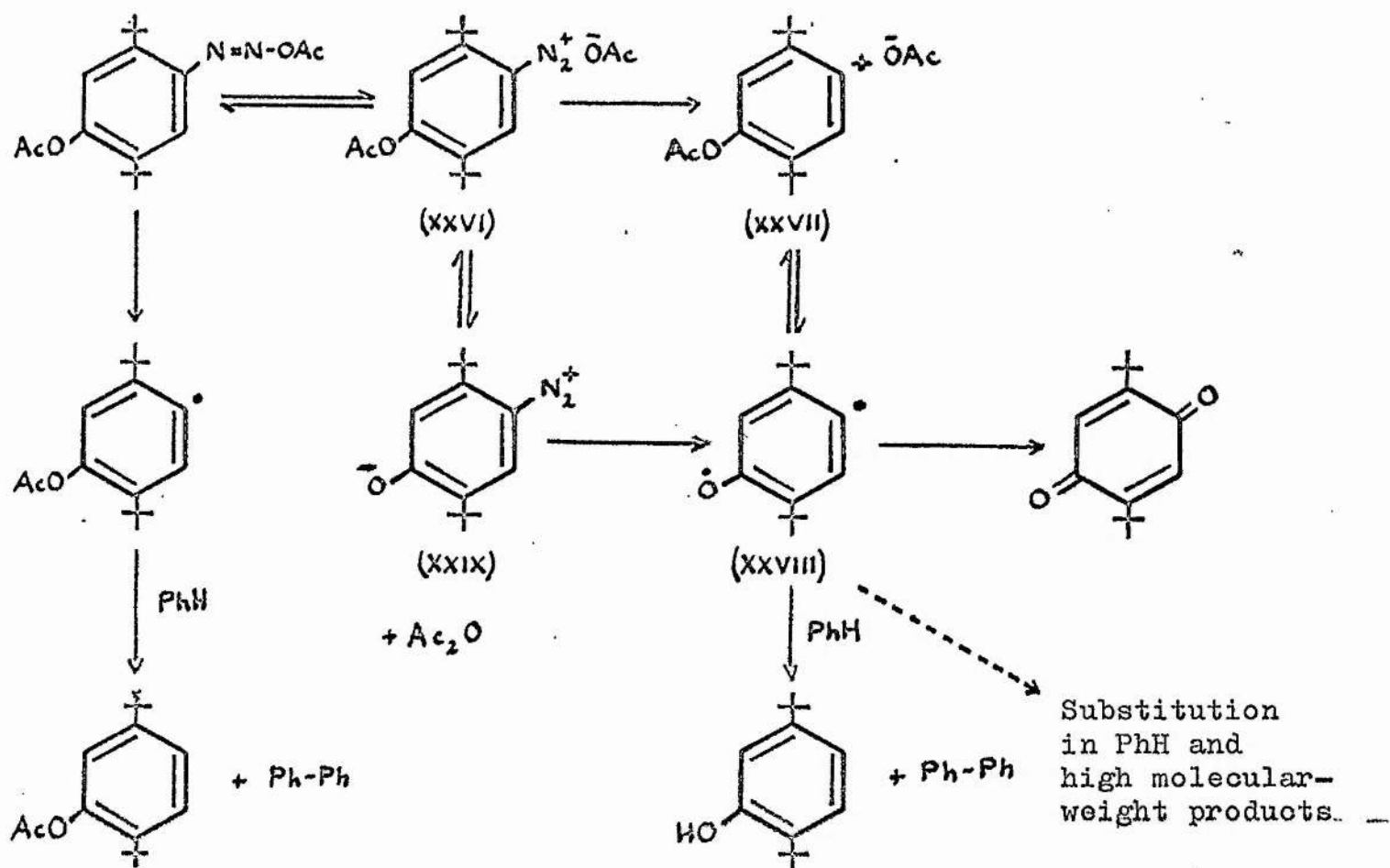
Nitrosobenzene was detected among the products of decomposition in benzene containing nitrobenzene (but not in pure nitrobenzene) and evidence was obtained for the formation of 2,6-dibromo-p-benzoquinone. The mechanism shown in Scheme 3 overleaf was suggested.

Any attempt to rationalise the formation of the products observed in the decomposition of 4-acetoxy-2,5-di-*t*-butyl-N-nitrosoacetanilide in benzene must be speculative since together they account for less than 16% of the nitrosamide, and might be merely by-products of the major reaction path. Scheme 4 overleaf, though incomplete, seems plausible.

Scheme 3



Scheme 4

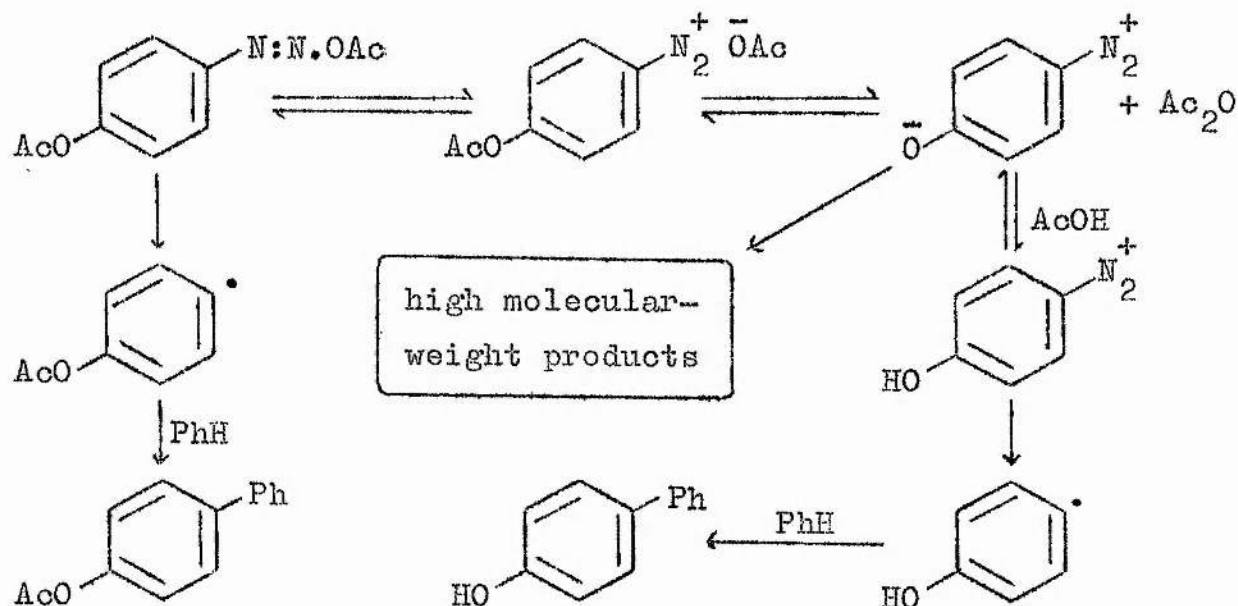


The formation of 2,5-di-*t*-butylphenyl acetate together with biphenyl is analogous to the production of (some of) the *p*-di-*t*-butylbenzene in the decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide. Deacylation of either diazonium (XXVI) or carbonium (XXVII) ions would result in acetic anhydride, which was detected (70-90m/100m) by g.l.c. Much of the diradical (XXVIII) and the diazo-oxide (XXIX) would end up as high molecular-weight material, although abstraction by the radical may be encouraged by the bulky *t*-butyl groups. While benzene could act as a source of hydrogen, the identity of the oxidising agent necessary for quinone formation is not obvious.

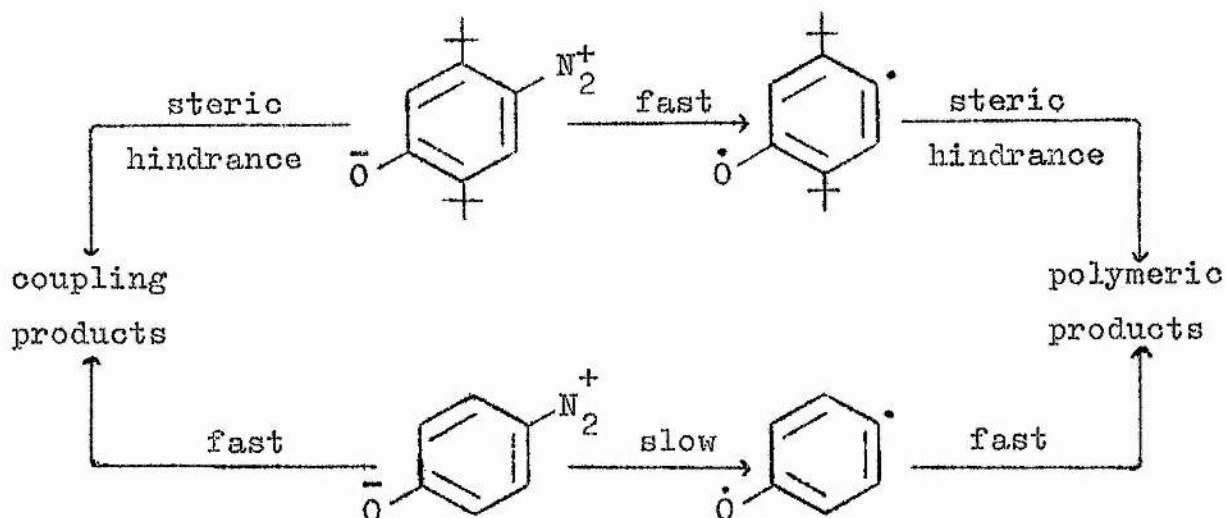
An attempt was made to obtain a higher accountability of starting material by allowing 4-acetoxy-2,5-di-*t*-butyl-N-nitrosoacetanilide to decompose in cyclohexane. As the results (p. 177) indicate, this was only marginally successful and provided no further useful information, although the task of isolating the decomposition products, and hence of confirming their identities, was somewhat simplified.

A brief investigation of the decomposition of *p*-acetoxy-N-nitrosoacetanilide in benzene, looking particularly for any evidence of deacylation, was undertaken. 4-Acetoxy-biphenyl (39.4m/100m) was the major reaction product, and while neither phenol nor *p*-benzoquinone were detected,

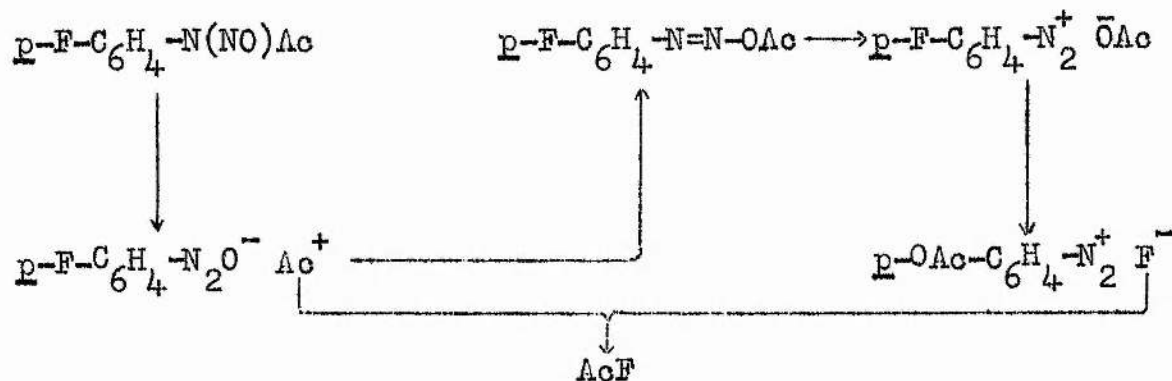
the formation of 4-hydroxybiphenyl (2.0m/100m) indicated that some deacylation had occurred.



Acetanilide (67m/100m nitrosamide) resulted when aniline was added to the reaction mixture, suggesting that a large proportion of the nitrosamide had, in fact, reacted by way of deacylation. The detection of so little deacetylated product, in contrast to the decomposition of 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide, probably reflects the great reactivity of benzene-1,4-diazo-oxide. The diagram below illustrates the (potentially) important effect of the presence of *t*-butyl groups in the diazo-oxide:

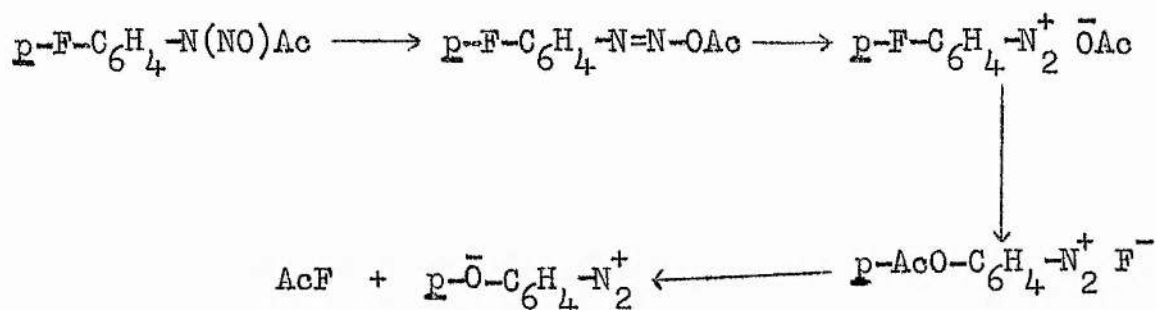


In formulating his recent modification of Rüchardt and Freudenberg's theory, Suschitzky<sup>143</sup> cited the formation of acetyl fluoride in the decomposition of p-fluoro-N-nitrosoacetanilide in benzene as evidence for heterolysis of the nitrosamide:

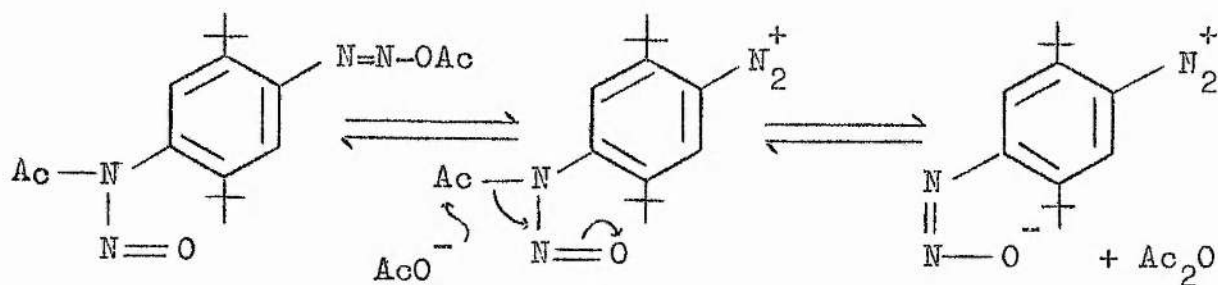


Perhaps the deacetylation of p-acetoxy-N-nitrosoacetanilide points to an alternative path to acetyl fluoride, not requiring heterolysis of the nitrosamide to an acylium cation:





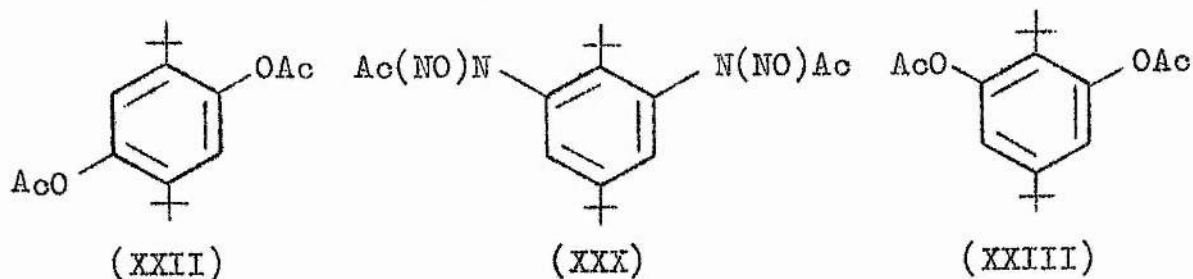
Investigation of the reactions of 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide thus provided valuable insight into the decomposition of 1,4-di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)-benzene. First, it demonstrated that even if 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide were formed initially, its subsequent reaction would not be as had been predicted. Secondly, since the yield of 2,5-di-*t*-butylphenol (5.1m/100m) from the acetoxynitrosamide exceeded that from the dinitrosamide (0.25m/100m) by a factor of twenty, it seemed unlikely that 1,4-di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene had initially formed the acetoxynitrosamide as a major product. Finally, it suggested that the complexity of the reactions of the dinitrosamide might be a consequence of marked interaction between the two nitrosamide functions, as for example:



It should be noted that no attempt was made to detect acetic anhydride in the reactions of the dinitrosamide.

2,5-Di-*t*-butyl-1,3-di-(*N*-nitrosoacetamido)benzene

Since complications in the reaction of 1,4-di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene probably result from interaction between the two nitrosamide functions, it was reasoned that the decomposition of the corresponding *m*-dinitrosamide (XXX) might be a simpler reaction, and should certainly afford a sample of 2,5-di-*t*-butylresorcinol diacetate (XXIII), whose absence from other reactions had been surmised rather than proven.



The identified decomposition products of 2,5-di-*t*-butyl-1,3-di-(*N*-nitrosoacetamido)benzene (XXX) in benzene, including biphenyl (6.8m/100m) and 2,5-di-*t*-butylphenyl acetate (4.8m/100m), accounted directly for only 6% of the dinitrosamide; and since no important product which could be detected (g.l.c.) remained unidentified, it was clear that this was by no means a simple reaction. 2,5-Di-*t*-butylresorcinol diacetate was formed, as predicted, but in

such low yield (0.6m/100m) as to prohibit its isolation in a pure state. The method of preparation of 1,3-diacetamido-2,5-di-t-butylbenzene (p.81) was such that the absence of traces of 1,4-diacetamido-2,5-di-t-butylbenzene could not be guaranteed. Thus the formation of a small amount of 2,5-di-t-butylhydroquinone diacetate (XXII, 0.4m/100m) is not necessarily indicative of aryne participation in the decomposition of 2,5-di-t-butyl-1,3-di-(N-nitrosoacetamido)-benzene. With cyclohexane as solvent, the yields of the two diacetates (2.0 and 1.2m/100m) and 2,5-di-t-butylphenyl acetate (13.7m/100m) were appreciably higher than in benzene, but no additional useful information was obtained.

The identity of the 2,5-di-t-butylresorcinol diacetate (XXIII) formed in these experiments was established as described below:

- a) A small quantity (17mg.) of material consisting of two components A (ca. 40%) and B (ca. 60%) was isolated (p. 173). The g.l.c. (NPGS capillary, 190°) retention time of A (16.0 min.) was identical to that of authentic 2,5-di-t-butylhydroquinone diacetate (XXII), and slightly shorter than that of B (16.6 min.).
- b) The n.m.r. spectrum of this material was compared with that of authentic 2,5-di-t-butylhydroquinone diacetate (XXII).

	<u>Aromatic</u>	<u>Methyl</u>	<u>t-Butyl</u>
(A + B) $\tau$	2.99, 3.16 (2H)	7.67, 7.70 (6H)	8.60, 8.67, 8.72 (18H)
(XXII) $\tau$	2.98 (2H)	7.67 (6H)	8.66 (18H)

All absorptions were singlet, and the peaks in the spectrum of (A + B) had integrals in the ratio expected for a mixture of (XXII) and 2,5-di-t-butylresorcinol diacetate (XXIII). The appearance of two t-butyl resonances in the spectrum of (A + B) in addition to that in the spectrum of (XXII) was consistent with the presence of (XXIII), in which the t-butyl groups are non-equivalent.

c) Further purification (p. 174) yielded component A, which had an i.r. spectrum indistinguishable from that of authentic 2,5-di-t-butylhydroquinone diacetate (XXII).

d) A trace of material containing approximately 70% of B was isolated and examined by mass spectroscopy. The more important peaks in the spectrum of this mixture and of authentic 2,5-di-t-butylhydroquinone diacetate (XXII) are recorded below.

(Abundances are approximate values, expressed as a percentage of the abundance of the ion with  $m/e$  222).

<u>m/e</u>	<u>Abundance(%)</u> <u>(XXII) (A + B)</u>		<u>m/e</u>	<u>Abundance(%)</u> <u>(XXII) (A + B)</u>		<u>m/e</u>	<u>Abundance(%)</u> <u>(XXII) (A + B)</u>	
306	5.4	10.6	179	2.2	9.5	77	4.7	7.2
291	0.5	2.5	177	2.3	2.9	69	4.1	4.3
264	14.5	33.5	175	1.2	2.3	67	5.6	5.4
249	2.8	7.5	165	3.8	5.7	57	19.0	33.5
231	0	1.3	163	4.0	6.4	55	9.0	9.5
222	100	100	105	4.2	5.8	43	55.0	67.1
207	51.1	109	91	7.0	9.8	41	23.0	27.9
191	8.9	14.6	79	4.2	6.3	39	8.9	9.8

The mass spectrum of the mixture, in which 2,5-di-*t*-butylhydroquinone diacetate was the minor component, contained only one important peak ( $m/e$  231) not present in the spectrum of pure (XXII), suggesting, though not proving, that the major component of the mixture was an isomer of (XXII).

The combined evidence from n.m.r. and mass spectroscopy was considered ample justification for assigning to component B the structure 2,5-di-*t*-butylresorcinol diacetate (XXIII).

Having isolated a specimen of 2,5-di-*t*-butylresorcinol diacetate (contaminated with the hydroquinone diacetate) it was possible to confirm that it was not a product of the

reactions of 1,4-di-*t*-butyl-2,5-di-(*N*-nitrosoacetamido)benzene and 4-acetoxy-2,5-di-*t*-butyl-*N*-nitrosoacetanilide.

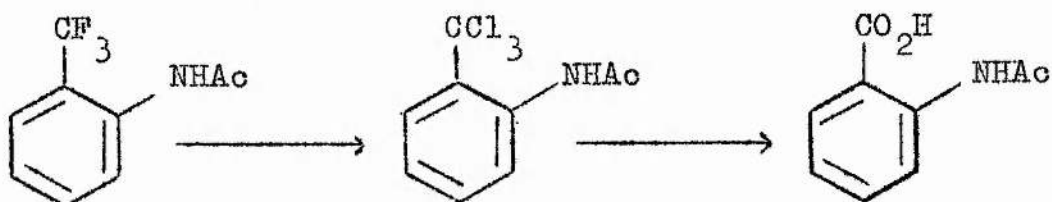
#### Other *o*-Substituted Acetylarlylnitrosamines

Confirmation of the anomalous behaviour of *o*-*t*-butyl-*N*-nitrosoacetanilide being a consequence of the bulky *o*-substituent might be forthcoming from an investigation of the reactions of acetylarlylnitrosamines with *o*-substituents of comparable size but dissimilar electronic character. An obvious choice, in spite of the inevitable synthetic difficulties, was *o*-trichloromethyl-*N*-nitrosoacetanilide.

Nitration of benzotrichloride with 30% nitric acid in sulphuric acid is reported by Scherer and Hahn<sup>212</sup> to give *m*-nitrobenzotrichloride in 90% yield, and although other workers<sup>213</sup> have suggested that a small amount (up to 7%) of *o*-nitrobenzotrichloride is formed, this isomer has not been isolated. Even if *o*-nitrobenzotrichloride were available, reduction of the nitro function without affecting the trichloromethyl group would not be readily accomplished.

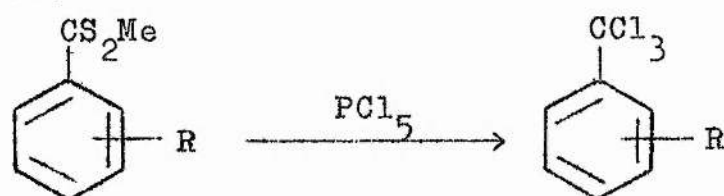
Henne and Newman<sup>172</sup> found that benzotrifluoride could not be acetylated under Friedel Crafts conditions with acetyl chloride and aluminium chloride; instead the product was benzotrichloride. More recently this procedure has been adapted to the preparation of 3-chloro-5-nitrobenzo-

trichloride and 3,5-dinitrobenzotrithloride.<sup>173</sup> Several attempts were made in the present investigation to convert o-trifluoromethylacetanilide into the trichloromethyl compound, but without success. Isolation of N-acetylanthranilic acid clearly indicated that reaction had occurred, but that the initial product had suffered hydrolysis:



No volatile material could be isolated when water was excluded from the work-up procedure.

Mayer and Scheithauer<sup>214</sup> have prepared a number of derivatives of benzotrithloride by treating the methyl ester of the corresponding dithiobenzoic acid with phosphorus pentachloride:

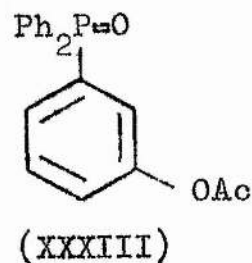
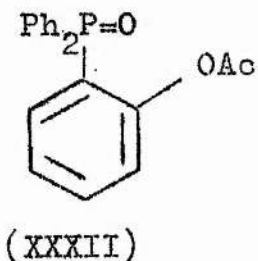
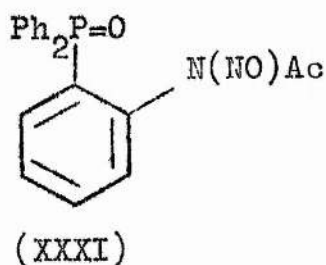


There seemed, however, little prospect of synthesising the dithioester and converting it into the trichloromethyl compound if the substituent R were an amino or acetamido group.

Attention was turned to other voluminous electron-attracting substituents, such as diphenylphosphinyl (Ph<sub>2</sub>P=O). o-Acetamidophenyldiphenylphosphine oxide was



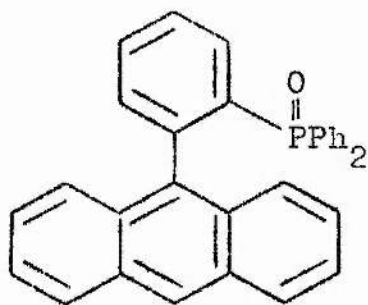
prepared, but subsequent nitrosation gave only partial conversion. Little information could be deduced from the decomposition of the impure nitrosamide (XXXI) in benzene, largely because of analytical difficulties. Both g.l.c.



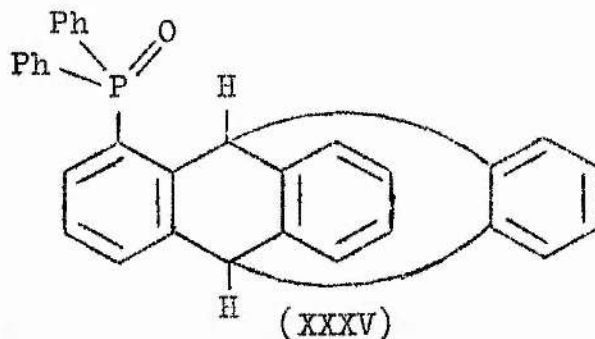
and distillation were excluded by the involatility of derivatives of triphenylphosphine oxide; while the polarity of the diphenylphosphinyl group necessitated the use of polar solvents (ether and alcohol) to elute any of the products from a chromatography column, with consequent poor separation and co-elution of tarry material. Although an authentic specimen of o-acetoxyphenyldiphenylphosphine oxide (XXXII) was prepared, the presence of the ester among the reaction products could not be unequivocally established; far less that of the m-acetate (XXXIII), of which no authentic sample was available.

The decomposition of nitrosamide (XXXI) in benzene containing anthracene afforded small amounts of two products, (XXXIV) and (XXXV), having similar melting points ( $228-9^{\circ}$  and  $227-8^{\circ}$ ) and elemental analyses, and the same molecular weight (454) determined by mass spectroscopy.

Although the i.r. spectra of both compounds contained a band that could be attributed to the P=O group (ca. 1200 cm.<sup>-1</sup>), they were clearly different, as also were the u.v. and n.m.r. spectra. Five long-wavelength absorptions (316, 332, 348, 365.5 and 384.5 mμ) characteristic of an anthracene derivative<sup>215</sup> were observed in the u.v. spectrum of (XXXIV), which resembled the spectrum of 9-phenylanthracene<sup>216</sup> more closely than that of the 1- or 2-substituted compound.<sup>217</sup> Moreover, since both theoretical calculation<sup>218</sup> and experimental observation<sup>38,127</sup> suggest that homolytic substitution will occur at position 9 in anthracene, this product (XXXIV) was assigned the structure 9-(o-diphenylphosphinylphenyl)anthracene.



(XXXIV)



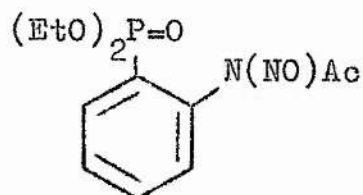
(XXXV)

Compound (XXXV), a structural isomer of (XXXIV), did not react with maleic anhydride indicating that the anthracene moiety had lost its dienic reactivity. Singlet absorptions in the n.m.r. spectrum ( $\tau$  3.81 and 4.56) at a higher field-strength than is usual for aromatic protons suggested the presence of bridge-head hydrogen atoms as in triptycene( $\tau$  4.6).<sup>156</sup>

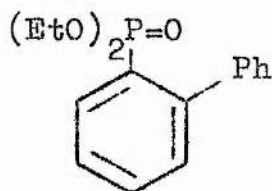
That one of these should be appreciably deshielded with respect to triptycene is consistent with the structure 1-diphenylphosphinyltriptycene for product (XXXV).

Despite the poor elemental analysis results (not uncommon for phosphorus-containing compounds) the evidence presented above is considered sufficient justification for the structural assignments made. Isolation of 1-diphenylphosphinyltriptycene appears to be excellent evidence for the participation of an aryne intermediate in the decomposition of diphenyl [o-(N-nitrosoacetamido)phenyl]phosphine oxide.

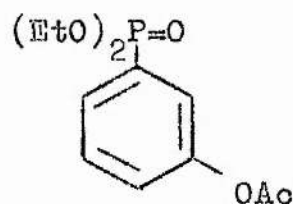
Although less voluminous and more flexible than the diphenylphosphinyl group, a diethoxyphosphinyl substituent is still bulky compared, for example, with the carbethoxy group. Further, since diethyl phenylphosphonate is more volatile than triphenylphosphine oxide, it seemed likely that the decomposition of diethyl o-(N-nitrosoacetamido)phenylphosphonate (XXXVI) would be both interesting and amenable



(XXXVI)



(XXXVII)



(XXXVIII)

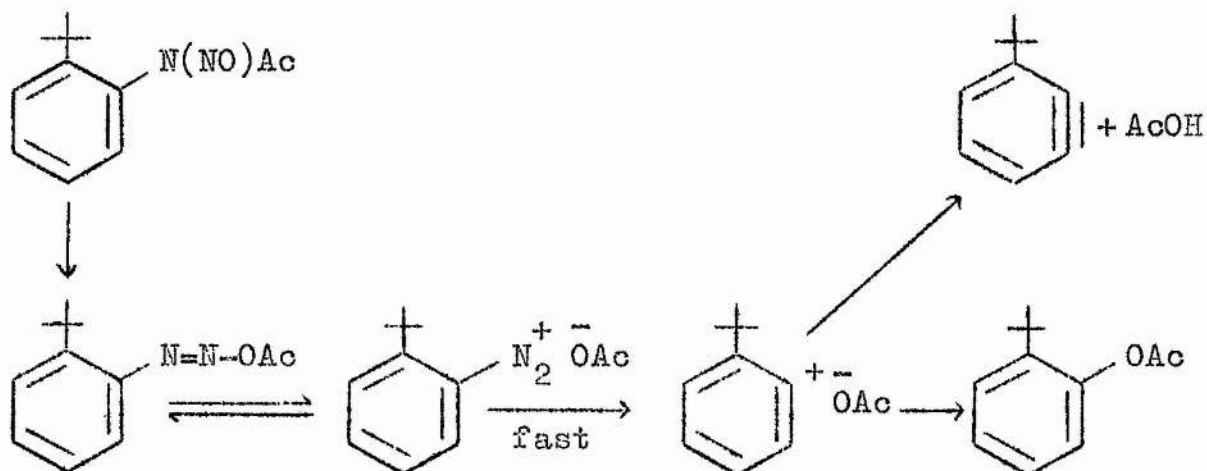
to examination by g.l.c. The major product from the decomposition in benzene was, however, diethyl 2-biphenyl-1-phosphonate (XXXVII, 22.8m/100m) formed by normal homolytic

substitution. The formation of a small amount of diethyl m-acetoxyphenylphosphonate (XXXVIII, 1.05m/100m) doubtless indicates some aryne participation; but without knowledge of the mechanism by which carboxylic acids add to benzyne, it is impossible to assess how much, if any, of the o-acetate (7.7m/100m) resulted from a dehydroaromatic intermediate. In many respects, including formation of the abstraction product, diethyl phenylphosphonate (4.6m/100m), accompanied by only a trace of biphenyl, this reaction is very similar to the decomposition of m-t-butyl-N-nitrosoacetanilide, and apart from the small yield of m-acetate, there is no justification for calling it anomalous.

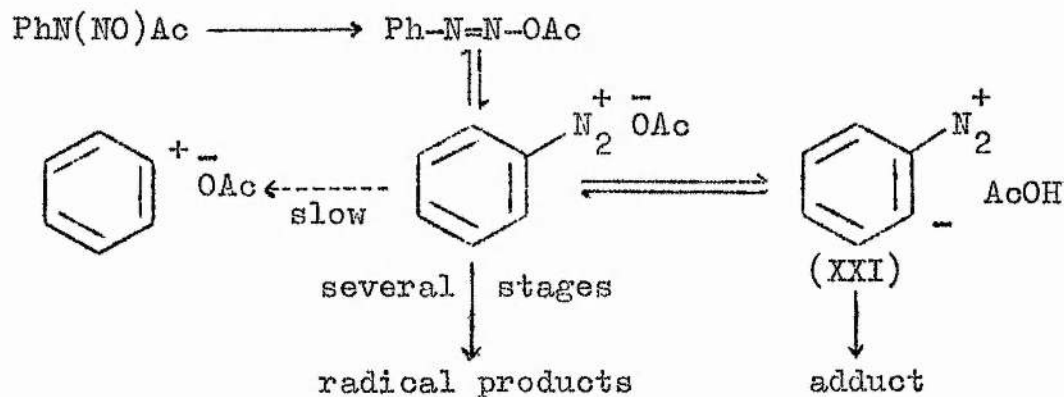
### Conclusions

The work described in this thesis has been concerned, for the most part, to establish the part played by aryne intermediates in the reactions of acetylarlylnitrosamines in benzene. Participation by 3-t-butylbenzyne in the decomposition of o-t-butyl-N-nitrosoacetanilide has been confirmed, and its rôle in the reaction investigated. In the absence of an arynophile this intermediate reacts with acetic acid to give m-t-butylphenyl acetate, but little, if any, of the o-isomer; while some t-butylbenzene may be formed by reduction of the aryne. The major decomposition

product, *o*-*t*-butylphenyl acetate, is doubtless formed largely from the aryl carbonium ion, which may also be a crucial intermediate in the generation of 3-*t*-butylbenzyne:



*N*-Nitrosoacetanilide and *m*- and *p*-*t*-butyl-*N*-nitrosoacetanilides do not appear to decompose by way of a true aryne, notwithstanding their formation of adducts with 2,3,4,5-tetraphenylcyclopentadienone. Having shown that an aryl radical, carbanion or carbonium ion is unlikely to be responsible for the adduct, it seems probable that the dipolar conjugate base of the aryldiazonium cation (e.g. XXI) is the arynoid intermediate:



The anomalous behaviour of o-t-butyl-N-nitrosoacetanilide might therefore be simply a consequence of steric strain in the diazonium cation causing rapid elimination of nitrogen. The results from this new investigation in no way confirm or disaffirm Cadogan and Hibbert's hypothesis<sup>8</sup> that the nitrosamide, because of its voluminous o-substituent, rearranges to the ois- (rather than the usual trans-) diazoacetate.

At least some of the t-butylbenzene formed by o-t-butyl-N-nitrosoacetanilide, and all that from the m- and p-isomers, arises by a non-aryne mechanism. While radical abstraction seems to be the likely path, the source of hydrogen, which possibly is not the same for the o-nitrosamide as for its m- and p-isomers, remains unidentified.

Of the other acetylarylnitrosamines investigated, only 2,5-di-t-butyl-N-nitrosoacetanilide decomposes to a considerable extent through an aryne intermediate, and even here most of the 2,5-di-t-butylphenyl acetate is formed from a carbonium ion. Results of experiments with 4-acetoxy-2,5-di-t-butyl-N-nitrosoacetanilide and p-acetoxy-N-nitrosoacetanilide suggest that complications in the decomposition of 1,4-di-t-butyl-2,5-di-(N-nitrosoacetamido)benzene arise from interaction between the nitrosamido functions. It is surprising, however, that the decomposition of 2,5-di-t-butyl-1,3-di-(N-nitrosoacetamido)benzene, in which the

N-nitrosoacetamido groups are meta to one another, should also be highly complex.

While the present investigation of substituted acetylaryl-nitrosamines was in progress, new information relating to the decomposition of unsubstituted N-nitrosoacetanilide in benzene became available. This has been referred to where relevant, but in general offers little assistance to comprehension of the rôle of either aryne or arynoid intermediates in the decomposition of acetylarylnitrosamines.

Some aryne participation was diagnosed in the reactions of diphenyl [o-(N-nitrosoacetamido)phenyl] phosphine oxide and diethyl o-(N-nitrosoacetamido)phenylphosphonate in benzene, although in the latter case the major product was the 'normal' biaryl. Much scope remains for studying the reactions of acetylarylnitrosamines with bulky o-substituents, although the formidable synthetic problems inherent in such work will not easily be solved.

In spite of the wealth of information already available, the nature and the rôle of each of the various reactive intermediates in the chemistry of acetylarylnitrosamines is not fully understood, and will doubtless continue to attract attention for many years to come.



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